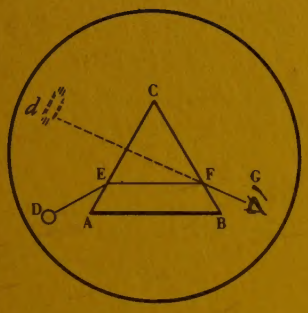

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CALCULATION OF $\overline{r^{-3}}(n, l)$ FROM THE FINE STRUCTURE OF SPECTRA

V. S. Korol'kov (pp. 137-140)

Received 31 August 1960

A convenient method is suggested for calculating $\overline{r^{-3}}(n,l)$ from the fine structure of energy levels. Several examples illustrate the method.

Calculation of nuclear magnetic and quadrupole mo-
s from the hyperfine structure of energy levels re-
s a knowledge of the parameter $\overline{r^{-3}}(n,l)$. Its value
e computed theoretically from the radial wave func-
, or found semiempirically from the fine structure
e energy levels.

As Eckert[1] has pointed out, calculation of $\overline{r^{-3}}(n,l)$
the theoretical radial wave functions can in some
s lead to considerable disagreement with experi-
al values. For example, the values of $\overline{r^{-3}}(3d)$ cal-
ed from Hartree-Fock wave functions for doubly
ed iron-group transition element atoms exceed by
ximately 20% the values calculated by Abragam
[2] from the hyperfine structure of the spectra.

The most usual way of determining $\overline{r^{-3}}(n,l)$ is by
the experimental spin-orbit coupling factors $\zeta_{n,l}$.
quantities $\zeta_{n,l}$ and $\overline{r^{-3}}(n,l)$ are related by[3]:

$$\zeta_{n,l} = hcR\alpha^2 Z_{\text{eff}} \cdot \overline{r^{-3}}(n, l). \qquad (1)$$

Equation (1) has the disadvantage of containing the
tive charge Z_{eff}, the choice of which is usually
what arbitrary.

We will represent the relationship between $\zeta_{n,l}$ and
,l) in a more convenient form by using easily calcu-
l coefficients. It is well known that[4]:

$$\zeta_{n,l} = \frac{hcR\alpha^2 a_0^3}{e}\left(\overline{\frac{1}{r}\frac{\partial U(r)}{\partial r}}\right), \qquad (2)$$

e U(r) is the potential of the field created by the
eus and all the electrons of the atom, and is regarded
aving central symmetry. We will write the potential
in the form:

$$U(r) = -\frac{Ze}{r} f(r), \qquad (3)$$

re f(r) is some function of r, the actual form of
h depends on the distribution of electron density
e atom. In a hydrogenlike atom, f(r) ≡ 1. For other
ns, f(r) may be represented explicitly by using some
nite atomic model. In the Thomas-Fermi atomic
el f(r) ≡ χ(x), where χ(x) is a universal function of
ument $x = 1.13\, Z^{1/3} r$ (for a table of this function, see
4, for example). In the self-consistent field model
≡ $Z_p(r)/Z$. Using Eq. (3), we average as in Eq. (2)
the radial wave function $P_N(n,l)$

$$\left[\overline{\frac{1}{r}\frac{\partial U(r)}{\partial r}}\right] = Ze\int_0^\infty \frac{1}{r^3}\left[f(r) - r\frac{df(r)}{dr}\right] P_N^2(n, l)\, dr. \qquad (4)$$

Since [f(r) − rdf(r)/dr] is a continuous function, and
·3)$P_N^2(n,l)$ nowhere changes sign, we can use the mean
ue theorem. As a result, we find:

$$\left[\overline{\frac{1}{r}\frac{\partial U(r)}{\partial r}}\right] = Ze\left[f(r') - r'\frac{df(r')}{dr}\right]\overline{r^{-3}}(n, l), \qquad (5)$$

re r′ is some fixed value of r.

We introduce the notation:

$$K(n, l; Z) = f(r') - r'\frac{df(r')}{dr}. \qquad (6)$$

The explicit form of the dependence of the coefficient K(n,l; Z) on Z can be determined only by the total electron density distribution in the atom in a region remote from both the nucleus and the boundaries of the atom. Applying the Thomas-Fermi statistical model to this region of the atom, it is possible to represent the function χ(x) to a good approximation by the equation*:

$$\chi(x) = 0.425 - 0.270 \ln x \quad (\text{for } 0.5 < x < 2.1). \qquad (7)$$

Experience in applying a statistical atomic model to the calculation of different properties of the atom has shown that when this model is used, a correct relationship is obtained between many properties and the atomic number. The method gives considerably less satisfactory numerical values for the different parameters characterizing atomic properties. Hence, substituting (7) in (6), we retain the coefficients only in terms depending on the atomic number, and we will not assign a numerical value to the constant term. We then obtain:

$$K(n, l; Z) = C(n, l) + 0.090 \cdot \ln \frac{\overline{r^{-3}}(n, l)}{Z}, \qquad (8)$$

where we put:

$$r' \sim [\overline{r^{-3}}(n, l)]^{-\frac{1}{3}}.$$

Taking (5) and (6) into consideration, we rewrite

*If we start with the self-consistent field model, it turns out that in the range of r of interest, the function Z_p/Z is also almost linear in ln r, while the coefficient of ln r is proportional to α, the slope constant introduced by Ridley (see ref. 5 for more details on α). Here, in the first approximation, the following equation applies:

$$\frac{Z_p}{Z} = \text{const} - 0.260 \ln r,$$

where the constant depends on the type of shell and the degree of ionization. Comparing this equation with Eq. (7), we conclude that the self-consistent field model should give the same results as the Thomas-Fermi model (except that the coefficients entering the equation will differ somewhat).

*Although the position of the point r′ will change with the atomic number, the ratio of r′ to $[\overline{r^{-3}}(n,l)]^{-1/3}$ will be almost invariant owing to the approximate geometrical similarity of the wave functions referring to the different atoms with the same unfilled shell (n,l).[5] This ratio enters Eq. (8) under the logarithm sign and thus its value will have little effect on K(n,l; Z).

Eq. (2) in the form:

$$\zeta_{n,l} = hcR\alpha^2 a_0^3 K(n, l; Z) Z\overline{r^{-3}}(n, l) \quad (9)$$

or, writing $\zeta_{n,l}$ in cm^{-1} and r(n,l) in atomic units, in the form:

$$\zeta_{n,l} = 5.84K(n, l; Z) Z\overline{r^{-3}}(n, l). \quad (9a)$$

Substituting (8) in (9a) gives:

$$\overline{r^{-3}}(n, l) = \frac{\zeta_{n,l}}{5.84Z} \cdot \left[C(n, l) + 0.09 \ln \frac{\overline{r^{-3}}(n, l)}{Z} \right]^{-1}. \quad (10)$$

Using this equation, it is easy to calculate the parameter $\overline{r^{-3}}(n,l)$ by successive approximations for all atoms with a given shell, if the value of $\overline{r^{-3}}(n,l)$ is known for one atom with this shell. The atom chosen should have only one electron outside the closed shell, since in this case the parameter $\overline{r^{-3}}(n,l)$ can be calculated either from Casimir's equation or from experimental values of the hyperfine splitting.[7] Where there is more than one electron outside the filled shell, there is no satisfactory way at present to calculate the parameter $\overline{r^{-3}}(n,l)$ from the hyperfine splitting.*

*This is because at present no theory has been developed enabling us to allow correctly for deviations from pure types of coupling (Russel-Saunders or j-j coupling) or for interconfigurational interaction.

As an example we will consider the calculation of $\overline{r^{-3}}(3d)$ for neutral atoms of the iron-group transition elements. We calculate K(3d, 21) from Eq. (9a) and obtain the value 0.461, using the value $\overline{r^{-3}}(3d) = 1.19$ (a.u.)$^{-3}$ for ScI, obtained in ref. 7 from the hyperfine structure. From the same equation, we calculate $\overline{r^{-3}}(3d)$ for all the remaining atoms with 3d shells, using K(3d; Z) = 0.461. We insert the values of $\overline{r^{-3}}(3d)$ obtained into the right hand side of Eq. (10) and obtain more exact values of $\overline{r^{-3}}(3d)$ (the process converges very rapidly). However, we must remember that the spin-orbit coupling factors have a large scatter in most cases. The effect of this is reduced as follows: Using the least squares method, we find coefficients a, b, c of the series:

$$[\overline{r^{-3}}(n, l)]^{\frac{1}{3}} = a + b(Z - Z_0) + c(Z - Z_0)^2 + \ldots, \quad (11)$$

where Z_0 is the atomic number of the element, corresponding to the average of the n,l shells. For the 3d shell of neutral atoms of the iron group, the series takes the form:

$$[\overline{r^{-3}}(3d)]^{\frac{1}{3}} = 1.542 + 0.114(Z - 25) - 0.001(Z - 25)^2 + \ldots.$$

The parabola constructed will be shifted somewhat relative to the chosen reference value. We shift it parallel to itself till it coincides with this reference value. In our example, the coefficient a must be reduced in value to 0.010. Table 1 shows the values of $\overline{r^{-3}}(3d)$ obtained in this way. These are final values. The same Table shows $\overline{r^{-3}}(3d)$ calculated from data on the hyperfine structure. The experimental values for copper are less accurate. More accurate values of $\overline{r^{-3}}(3d)$ were determined in ref. 7. It is easily seen that the agreement between the semiempirical calculation and the experimental results is very satisfactory. Table 2 shows calculations of $\overline{r^{-3}}(2p)$. The value $\overline{r_{2p}^{-3}} = 0.807$ (a.u.)$^{-3}$ for the neutral BI atom[7] was used as the reference value. The data given show that the values obtained are a little higher (5 to 10%) than the values obtained by calculating $\overline{r^{-3}}(2p)$ from the self-consistent field wave functions with exchange.[5]

Table 1. $\overline{r^{-3}}(3d)$ for Neutral Atoms of the Iron Group of Transition Elements

Element		$\overline{r^{-3}}(3d)$ (a.u.)$^{-3}$	
Z	Symbol	Calc.	Exper
21	Sc	1.19	1.19 [7]; 1.2 [2]
22	Ti	1.64	—
23	V	2.20	2.3 [2]
24	Cr	2.86	—
25	Mn	3.58	—
26	Fe	4.45	—
27	Co	5.41	5.2 [2]
28	Ni	6.49	—
29	Cu	7.65	8.0 [7]; 7.45 [2]

Table 2. $\overline{r^{-3}}(2p)$ Calculated Using the Semiempirical Method I and the Hartree-Fock Wave Function II

Element		$\overline{r^{-3}}(2p)$ (a.u.)$^{-3}$	
Z	Symbol	Calc. I	Calc. II
5	B	0.807	—
6	C	1.76	1.69
7	N	3.26	3.08
8	O	5.48	4.98
9	F	8.55	—

Therefore, representing the spin-orbit coupling factor by Eq. (9a) gives an easy and quite accurate calculation of the relative sizes of the given atomic shells, which is of great practical importance. In giving a concrete form to the function K(n,l; Z), we utilized only those parts of the Thomas-Fermi method which relate to the dependence of K(n,l; Z) on the atomic number. All of the remaining data were experimental. This enabled us to obtain quite accurate results.

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RECURRENCE FORMULAS IN THE CALCULATIONS OF MOMENTS OF DISTRIBUTIONS OF TRANSITION PROBABILITIES

O. I. Sil'd (pp. 141-145)

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Recurrence formulas are derived for the calculation of operators used for the determination of the moments of the distribution of transition probabilities in a quantized system. The application of the derived formulas is illustrated by the solution of certain problems: the energy spectrum and the transition probabilities of the harmonic oscillator are calculated; rules are derived which are analogous to the known theorem concerning the sum of the oscillator strengths; a scheme is given for the calculation of the moments of an electronic-vibrational band in the energy representation.

The method of moments suggested by Lax[1] proved to very effective in the calculation of the shape of continuous bands in electronic-vibrational spectra belonging impurities in crystalline phosphors and to complex ecules.[2-9] The description of the distribution of spec- intensities by the method of moments is also useful ther problems.[8] The purpose of this note is the deri- on of certain mathematical relationships for the cal- tion of the moments of the distribution of transition abilities in an arbitrary quantized system. Recur- e formulas are obtained for operators used for the ulation of the moments, and examples are given of r application to various quantized systems.

The moment of order l of the distribution of transi- probabilities in terms of the transition energies is n for an arbitrary quantized system by[8]

$$S_l = \sum_f (E_f - E_i)^l W_{fi}, \tag{1}$$

re $W_{fi} = |\int \Psi_f^* (\hat{P}\Psi_i)\, d\tau|^2$ is the probability (to within onstant factor) of the transition of the system from state i to the state f; E_i and E_f are the energies hese states; $\hat{P}$ is the perturbation operator producing transition; Ψ_p is the wave function of the stationary e p.

Let us substitute into Eq. (1), written in the form

$$S_l = \sum_f (E_f - E_i)^l \int \Psi_f (\hat{P}\Psi_i)^*\, d\tau \int \Psi_f^* (\hat{P}\Psi_i)\, d\tau,$$

place of E_i and E_f, the Hamiltonian operators of the ial and final states of the system $\hat{H}_I$ and $\hat{H}_{II}$. By not uming for the time being that $\hat{H}_I = \hat{H}_{II}$, we retain the sibility of using them in various approximations. ce the operators $\hat{H}_I$ and $\hat{H}_{II}$ are self-conjugate, the ment S_l can be represented as

$$S_l = \sum_f \int \Psi_f (\hat{Q}_l \Psi_i)^*\, d\tau \int \Psi_f^* (\hat{R}_l \Psi_i)\, d\tau, \tag{2}$$

ere $\hat{Q}_l$, $\hat{R}_l$ are linear combinations of the operators the type $\hat{H}_{II}^k \hat{P} \hat{H}_I^p$, and where $\hat{Q}_0 = \hat{R}_0 = \hat{P}$.

The moment S_{l+1} can be written in the form

$$S_{l+1} = \sum_f (E_f - E_i) \int \Psi_f (\hat{Q}_l \Psi_i)^*\, d\tau \int \Psi_f^* (\hat{R}_l \Psi_i)\, d\tau.$$

Substitutions of $E_p \to \hat{H}$ in the last equation give

$$(E_f - E_i) \int \Psi_f (\hat{Q}_l \Psi_i)^*\, d\tau = \int \Psi_f (\hat{H}_{II} \hat{Q}_l - \hat{Q}_l \hat{H}_I)^* \Psi_i^*\, d\tau$$

$$(E_f - E_i) \int \Psi_f^* (\hat{Q}_l \Psi_i)\, d\tau = \int \Psi_f^* (\hat{H}_{II} \hat{R}_l - \hat{R}_l \hat{H}_I) \Psi_i\, d\tau.$$

Using the completeness condition of the system of wave functions Ψ_f, which has the form $\sum_f \Psi_f^*(\tau')\Psi_f(\tau) = \delta(\tau' - \tau)$, we carry out the summation over f. We finally obtain

$$S_l = \int (\hat{Q}_l \Psi_i)^* (\hat{R}_l \Psi_i)\, d\tau. \tag{3}$$

For $\hat{Q}_1$ and $\hat{R}_1$ in Eq. (3) the following relationships hold:

$$\hat{Q}_{l+1} = \hat{H}_{II} \hat{Q}_l - \hat{Q}_l \hat{H}_I; \quad \hat{R}_{l+1} = \hat{R}_l \tag{4a}$$

or

$$\hat{Q}_{l+1} = \hat{Q}_l; \quad \hat{R}_{l+1} = \hat{H}_{II} \hat{R}_l - \hat{R}_l \hat{H}_I, \tag{4b}$$

where $\hat{Q}_0 = \hat{R}_0 = \hat{P}$.

The expressions (4) are the recurrence formulas for the operators $\hat{Q}_l$ and $\hat{R}_l$ which determine the moments S_l with the help of Eq. (3). $\hat{Q}_l$ is here a linear combination of operators of the type $\hat{H}_{II}^k \hat{P} \hat{H}_I^p$. If $\hat{P}$ is a self-conjugate operator, then the relationship

$$\int (\hat{H}_{II}^k \hat{P} \hat{H}_I^p \Psi_i)^* (\hat{R}_l \Psi_i)\, d\tau = \int \Psi_i^* (\hat{H}_I^p \hat{P} \hat{H}_{II}^k \hat{R}_l) \Psi_i\, d\tau.$$

holds.

This allows us to consider the moment S_l as the average value of the operator $\hat{S}_l$ in the state i, that is,

$$S_l = \int \Psi_i^* \hat{S}_l \Psi_i\, d\tau. \tag{5}$$

The quantity $\hat{S}_l = \hat{Q}_l \hat{R}_l$ will be called the momentum operator, with the recurrence formulas for $\hat{Q}_l$ and $\hat{R}_l$ having in this case the form

$$\hat{Q}_{l+1} = \hat{Q}_l \hat{H}_{II} - \hat{H}_I \hat{Q}_l; \quad \hat{R}_{l+1} = \hat{R}_l \tag{6a}$$

or

$$\hat{Q}_{l+1} = \hat{Q}_l; \quad \hat{R}_{l+1} = \hat{H}_{II} \hat{R}_l - \hat{R}_l \hat{H}_I, \tag{6b}$$

where $\hat{Q}_0 = \hat{R}_0 = \hat{P}$.

In this particular case $\hat{H}_I = \hat{H}_{II}$ and

$$\hat{Q}_{l+1} = i\hbar \frac{d\hat{Q}_l}{dt}; \quad \hat{R}_{l+1} = \hat{R}_l \tag{7a}$$

or

$$\hat{Q}_{l+1} = \hat{Q}_l; \quad \hat{R}_{l+1} = -i\hbar \frac{d\hat{R}_l}{dt}. \tag{7b}$$

Thus the recurrence formulas (6) and (7) are obtained for the determination of the momentum operator

$\hat{S}_1$, and the mean values of $\hat{S}_1$ according to (5) give the necessary moments.

The application of the recurrence formulas will now be illustrated by a few examples.

1. The Harmonic Oscillator. The Hamiltonian operator has the form

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2,$$

where m and ω are the mass and the frequency of the oscillator, respectively. The perturbation operator is $\hat{P} = x$ (dipole transition). According to (6b) with $\hat{H}_I = \hat{H}_{II}$ we have

$$\hat{R}_l = (\hbar\omega)^2 \hat{R}_{l-2},$$

with

$$\hat{R}_0 = x, \quad \hat{R}_1 = -\frac{\hbar^2}{2m} 2\frac{d}{dx}; \quad \hat{Q}_l = \hat{Q}_0 = x.$$

The moments are

$$S_l = (\hbar\omega)^2 S_{l-2},$$

with

$$S_0 = \langle x^2\rangle_{ii}, \quad S_1 = \frac{\hbar^2}{2m}.$$

The quantity $\langle\hat{O}\rangle_{ii}$ denotes the mean value of the operator $\hat{O}$ in the state i.

It follows from the virial theorem that the mean values of the kinetic and potential energies of a harmonic oscillator are equal. Therefore

$$\left\langle \frac{m\omega^2}{2} x^2 \right\rangle_{ii} = \frac{E_i}{2}, \quad S_0 = \langle x^2\rangle_{ii} = \frac{E_i}{m\omega^2},$$

where E_i is the total energy of the oscillator in the state i.

Finally,

$$\left.\begin{aligned} S_l &= (\hbar\omega)^l \frac{E_i}{m\omega^2} && \text{if } l \text{ — is even,} \\ \text{and} \\ S_l &= (\hbar\omega)^{l-1}\frac{\hbar^2}{2m}, && \text{if } l \text{ — is odd.} \end{aligned}\right\} \quad (8)$$

It follows from Eq. (8) that the dipole transition of a harmonic oscillator takes place without dependence on the initial level only between energy levels which are at a distance $\hbar\omega$ from each other. Consequently, the spectrum of the energy levels of a harmonic oscillator consists of a series of equidistant lines (at a distance $\hbar\omega$ from each other).

The zeroth moment $S_0 = E_i/m\omega^2 = \sum_f W_{fi} \geq 0$, and therefore there are only positive energy values of a harmonic oscillator, i.e., $E_i \geq 0$. For the lowest (zeroth) level

$$S_0 = \frac{E_0}{m\omega^2}, \quad S_1 = \hbar\omega S_0 = \frac{\hbar^2}{2m}.$$

Therefore, the value for the zero-energy of a harmonic oscillator is

$$E_0 = \frac{\hbar\omega}{2}.$$

Since the dipole transitions occur only to the adjacent energy levels, the moments S_0 and S_1 determine the sum and the difference of the probabilities of these transitions and thus the probabilities themselves, i.e.,

$$W_{i+1,\,i} = \frac{i+1}{2m\omega^2}\hbar\omega,$$

$$W_{i-1,\,i} = \frac{i}{2m\omega^2}\hbar\omega.$$

Thus, by calculating the moments of the distribution of transition probabilities, we have obtained the well known results concerning the energy spectrum, the selection rule, and the transition probabilities. It was not necessary for this purpose to solve the Schrödinger equation.

2. The Atom. The perturbation operator is the projection of the dipole moment of the atom along the direction of the electric vector of the light wave. $\hat{P} = \sum_k x_k$, where x_k is the x-coordinate of the kth electron in the atom. By using the Ehrenfest theorem, we obtain by means of Eq. (7) the first moments of the distribution of the transition probabilities

$$\left.\begin{aligned} S_0 &= \sum_k\sum_n \langle x_k x_n\rangle_{ii}, \\ S_1 &= -\frac{i\hbar}{m}\sum_k\sum_n \langle x_k \hat{p}_{xn}\rangle_{ii}, \\ S_2 &= \frac{\hbar^2}{m^2}\sum_k\sum_n \langle \hat{p}_{xk}\hat{p}_{xn}\rangle_{ii}, \\ S_3 &= -i\hbar\frac{\hbar^2}{m^2}\sum_k\sum_n \left\langle \frac{\partial U}{\partial x_k}\hat{p}_{xn}\right\rangle_{ii}, \\ S_4 &= \frac{\hbar^4}{m^2}\sum_k\sum_n \left\langle \frac{\partial U}{\partial x_k}\frac{\partial U}{\partial x_n}\right\rangle_{ii}, \end{aligned}\right\} \quad (9)$$

where $\hat{p}_{xk}$ is the operator of the projection of the momentum of the kth electron along the direction of the electric vector of the light wave, and U is the potential energy of the atom. The moments S_2, S_3, and S_4 in Eq. (9) agree with the corresponding sum rules by Vinti,[10] obtained by a different method.

The first moment of the distribution

$$W'_{fi} = \frac{2m}{\hbar^2}\left|\sum_k\int \Psi_f^* x_k \Psi_i\, d\tau\right|^2$$

represents the sum of the oscillator strengths for transitions from state i to state f:

$$\hat{S}_1 = -2\sum_k\sum_n \left\langle x_k\frac{\partial}{\partial x_n}\right\rangle_{ii} = N, \quad (10)$$

where N is the number of electrons in the atom. Equation (10) expresses the well known theorem on the sum of oscillator strengths.[11]

It is easy to go beyond the dipole approximation and to generalize Eqs. (9) and (10).

3. The Electronic-Vibrational Transition in the Condon Approximation. For the calculation of the moments of the distribution of transition probabilities for a given electronic transition in an adiabatic approximation, the perturbation operator is the electronic matrix element of this transition M (see ref. 8).

The expressions for the moments of the electronic-vibrational band in the Condon approximation (M = const) have, according to (5) and (6), the following form

$$S_{l\alpha} = \int \varphi_\alpha^* \hat{S}_l \varphi_\alpha\, d\tau, \quad (11)$$

$$\left.\begin{aligned} \hat{S}_{l+1} &= \hat{H}_{II}\hat{S}_l - \hat{S}_l\hat{H}_I, \\ \hat{S}_0 &= M^2 = \text{const}, \end{aligned}\right\} \quad (12)$$

φ_α is the vibrational wave function of the initial tional state α; $\hat{H}_I$ and $\hat{H}_{II}$ are the Hamiltonian op- rs describing the vibrations of the nuclei in the and final states, respectively.

ince the necessary moments are, according to 1), the mean values of the moment operator $\hat{S}_1$ in itial state, it is useful to conduct the calculations he help of Eq. (12) in the energy representation esponding to the vibrational states of the initial ronic state). The diagonal element number α of the x S_1 is then the moment $S_{1\alpha}$ for the transition from itial vibrational state α.

or a simultaneous calculation of the transitions all the vibrational states α, it is necessary to ge the moments $S_{1\alpha}$ (diagonal elements of the $\hat{S}_1$ x) with the distribution function of the system over ates α. Such averaging of the matrix elements ers) is simpler than the averaging of the distribu- of coordinates of the system in the states α (aver- of functions), which is carried out in the calcula- f the moments in the coordinate representation for taneously taking account of transitions from all vi- nal states.[9]

n this manner, the calculation of the moments S_1 of an electronic-vibrational band was made in the l case of a model of a single anharmonic oscillator, ans of Eq. (12) in the energy representation, in or- take into account the effect of the anharmonicity rations in the initial electronic state.[9] The calcula- f the moments of an electronic-vibrational band, energy representation, for more complex models (for instance, for a system of anharmonic oscillators) is the subject of a separate paper.

In conclusion, I express my sincere gratitude to K. K. Rebane for the direction of the present work.

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HEORY OF INFRARED ABSORPTION BAND INTENSITIES OF COMPLEX MOLECULES CONTAINING SEVERAL IDENTICAL GROUPS

L. A. Gribov (pp. 146-150)

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The problem of the dependence of infrared absorption band intensities on the number of identical groups in complex molecules has been theoretically considered on the basis of the valence-optical scheme. A comparison of the theory with the experimental data in the $(CH_3)_nSiCl_{4-n}$ series has been carried out.

The problem of determining the number of identical acteristic chemical groups (for example, CH, CH_2, NH, etc.) in complex molecules is one of the im- nt problems of analytical chemistry. The method of red spectroscopy renders substantial assistance in olution of such questions, a method which, as is well n, is extremely sensitive to variations of any kind in tructure of the molecule. In particular, it has been blished that a change in the number of identical ps in the molecule is accompanied, in the majority ses, by a very pronounced increase or decrease in ntensities of the corresponding absorption bands. ever, the experimental material collected at the pres- ime does not suffice to reveal any general regulari- of this sort in the spectra of polyatomic molecules. true that a number of investigators adhere to a be- n a linear dependence of the intensities on the num- of equivalent groups. Even without speaking of the that this assumption often contradicts the experi- al data, we note that, in doing so, they completely fail to take account of the effect, if any, of the symmetry of the molecule.

A correct answer to the question posed can be given only on the basis of a systematic theoretical investigation. The particular case of n equivalent bonds forming equal angles with one another has previously been examined by Vol'kenshtein.[1] In the present work, an attempt is made to solve the problem in general form on the basis of valence-optical theory (see also ref. 2).

As is well known,[3] the integrated intensity of the absorption band corresponding to the i-th normal vibration equals

$$I_i = \frac{N\pi}{3c}\left|\left(\frac{\partial\mu}{\partial Q_i}\right)_0\right|^2,$$

where N is the total number of molecules in a unit volume and $(\partial\mu/\partial Q_i)_0$ is the derivative of the dipole moment of the molecule with respect to the given normal coordinate.

From the general formula for the change in the di-

pole moment vector of a molecule during a vibration (see refs. 4 and 5), we obtain

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0=\left[\{\mathbf{e}\}\left|\frac{\partial\mu}{\partial q}\right|+\{\mu\}\,S^{-1}\,(\Delta\varepsilon B T-\mathbf{E})\right]\cdot\|q\|_i\frac{\nu_i}{\sqrt{\{q_i\}\,U\,\|q_i\|}}. \tag{1}$$

Here and below, the same symbols are adopted as in refs. 4 and 5.

Let us now consider a molecule consisting of some unchanging common part (let us call it the nucleus), to which n identical groups of atoms are attached. The intensity of the absorption band corresponding to some normal vibration of the molecule will be determined both by the vibrations of the nucleus and by the vibrations of the groups under consideration. Furthermore, as the number of equivalent groups increases, the electrical and mechanical parameters of the molecule, and the forms and frequencies of the vibrations, may undergo pronounced changes. Therefore, in the general case, the dependence of the intensities of corresponding absorption bands on the number of equivalent groups may prove to be very complex and irregular.

The problem is simplified, however, if one investigates vibrations which are characteristic in frequency and in form for the equivalent groups; i.e., if one assumes that the equilibrium geometric parameters of the nucleus do not change in a given normal vibration.

Let us designate the sets of quantities (groups of internal vibrational coordinates, submatrices of the **B**, T, and $|\partial\mu/\partial q|$ matrices, etc.) which refer to the n separate groups by the indices 1, 2, ..., n, and the sets of the same quantities for the nucleus by the index 0. Let us further suppose that the submatrices $(\partial\mu_k/\partial q_l)$ and U_{kl} for $k\neq l$ and k,l = 1, 2, ..., n are equal to zero; i.e., that the force and electrical fields of the groups under consideration do not overlap. Such assumptions are entirely consistent with ordinary experimental practice.

Taking account of all that has been said, let us write formula (1) in the form

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0=\left[\{\mathbf{e}_1,\ \ldots,\ \mathbf{e}_n,\ \mathbf{e}_0\}\begin{vmatrix}\frac{\partial\mu_1}{\partial q_1}&\cdots&0&\frac{\partial\mu_1}{\partial q_0}\\ \cdots&\cdots&\cdots&\cdots\\ 0&\cdots&\frac{\partial\mu_n}{\partial q_n}&\frac{\partial\mu_n}{\partial q_0}\\ \frac{\partial\mu_0}{\partial q_1}&\cdots&\frac{\partial\mu_0}{\partial q_n}&\frac{\partial\mu_0}{\partial q_0}\end{vmatrix}\right.$$

$$\left.+\{\mu_1,\ \ldots,\ \mu_n,\ \mu_0\}\right]$$

$$\times\begin{vmatrix}S_1^{-1}&\cdots&0\\ \cdots&\cdots&\cdots\\ 0&\cdots&S_n^{-1}0\\ 0&\cdots&0\,S_0^{-1}\end{vmatrix}\left(\begin{vmatrix}\Delta\varepsilon_1&&\\ &\ddots&\\ &&\Delta\varepsilon_n\\ &&\Delta\varepsilon_0\end{vmatrix}\{\tilde{\mathbf{B}}_1,\ \ldots,\ \tilde{\mathbf{B}}_n,\ \tilde{\mathbf{B}}_0\}\begin{vmatrix}\tau_{11}&\cdots&\tau_{1n}\tau_{10}\\ \cdots&\cdots&\cdots\\ \tau_{n1}&\cdots&\tau_{nn}\tau_{n0}\\ \tau_{01}&\cdots&\tau_{0n}\tau_{00}\end{vmatrix}\right.$$

$$\left.-\begin{vmatrix}\mathbf{E}_1&\cdots&0\\ \cdots&\cdots&\cdots\\ 0&\cdots&\mathbf{E}_n0\\ 0&\cdots&0\mathbf{E}_0\end{vmatrix}\right)\left\|\begin{matrix}q_1\\ \vdots\\ q_n\\ 0\end{matrix}\right\|_i\frac{\nu_i}{\sqrt{\sum_k^n\{q_k\}_i U_{kk}\,\|q_k\|_i}}$$

$$=\frac{\nu_i}{\sqrt{\sum_k^n\{q_k\}_i U_{kk}\,\|q_k\|_i}}$$

$$\times\left\{\left(\sum_k^n\left[\{\mathbf{e}_k\}\left|\frac{\partial\mu_k}{\partial q_k}\right|+\{\mu_k\}\,S_k^{-1}\left(\Delta\varepsilon_k\tilde{\mathbf{B}}_k\theta_{kk}^{-1}-\mathbf{E}_k\right)\right]\|q_k\|_i\right)\right.$$

$$\left.+\text{interaction terms}\right\}, \tag{2}$$

where θ_{kk} is the submatrix of the T^{-1} matrix composed of the elements of the k-th equivalent group. The interaction terms include all the corrections to $(\partial\mu/\partial Q)_0$ of the molecule which appear by virtue of the electrical coupling of each equivalent group with the nucleus of the molecule; i.e., the difference from zero of the elements of the $|\partial\mu_0/\partial q_k|$ submatrices, the noninvariance of the T_{kk} submatrices referring to molecules with different numbers of groups, the possible rotations in space of the nucleus as a whole during vibrations within the functional groups under consideration, and also the corrections to the deflections of the bonds of these groups which arise by virtue of the requirement that the center of mass and the angular momentum of the whole molecule must be preserved during a vibration of a given form. A more detailed exposition of the physical meaning of the interaction terms, their form, and the methods of calculating them are presented in ref. 6.

In those cases when the interaction terms may be neglected, formula (2) will take the form

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0=\frac{\nu_i}{\sqrt{\sum_k^n\{q_k\}_i U_{kk}\,\|q_k\|_i}}\cdot\sum_k^n(\mathfrak{E}_k\cdot\|q_k\|_i),$$

where

$$\mathfrak{E}_k=\left[\{\mathbf{e}_k\}\left|\frac{\partial\mu_k}{\partial q_k}\right|+\{\mu_k\}\,S_k^{-1}\left(\Delta\varepsilon_k\tilde{\mathbf{B}}_k\theta_{kk}^{-1}-\mathbf{E}_k\right)\right].$$

However, the dependence of $(\partial\mu/\partial Q_i)_0$ on the number of identical groups in the molecule may even then prove to be very complex (even when the values of $\mathfrak{E}_k$ and U_{kk} are preserved), since on going from one molecule to another both the frequency of the vibration and the forms $\|q_k\|$ may change. Nevertheless, formula (3) may serve, even under these conditions, for the calculation of estimates. In the simplest case, when the forms $\|q_k\|$ differ from one another by a constant factor ($\|q_k\|_i=\alpha_k\|q\|_i$), we have

$$\left(\frac{\partial\mu}{\partial Q_i}\right)_0=\frac{1}{\sqrt{\{q\}_i\,U_{kk}\,\|q\|_i}}\cdot\frac{\nu_i}{\sqrt{\sum_k^n\alpha_k^2}}\cdot\sum_k^n(\alpha_k\mathfrak{E}_k\|q\|_i).$$

Let us represent the vector $\mathfrak{E}_k\|q_k\|$ in the form $A_k\mathbf{h}_k$, where $\mathbf{h}_k$ is the unit directional vector and A_k is the absolute magnitude of the vector $\mathfrak{E}_k\|q_k\|$. Since we are dealing with groups identical in structure, then $U_{kk}=U$ for all k, and $A_k=A$.

Let us suppose further that the $\mathfrak{E}$ and U matrices and the form $\|q\|$ are preserved in the series of molecules under investigation, and also that the condition that the interaction terms be small is always fulfilled. In other words, there will be constant specificity of the $\mathfrak{E}_k\|q\|$ vectors of the equivalent groups. Then the dependence of the intensity of a normal vibration on the number of identical groups in the molecule will be expressed by the simple formula

$$I_i(n)=\frac{N\pi}{3c}\cdot\frac{A^2}{(\{q\}_i\,U\,\|q\|_k)}\cdot\frac{\nu_i^2(n)}{\sum_k^n\alpha_k^2}\cdot\left(\sum_k^n\alpha_k\cdot\mathbf{h}_k\right)^2$$

$$=\text{const}\cdot\frac{\nu_i^2(n)}{\sum_k^n\alpha_k^2}\cdot\left(\sum_k^n\alpha_k\cdot\mathbf{h}_k\right)^2.$$

n the other hand, if it is found experimentally that tensity of some band in the series of molecules is t to this rule, then this may serve as a strong argu- in favor of the preservation of the form of the vi- n and of the electro-optical parameters of the s under study. We note that, in the case of degener- orations,

$$I = \frac{N\pi}{3c} \sum \left(\frac{\partial \mu}{\partial Q}\right)_0^2,$$

the summation is carried out over all components degeneracy. The dependence of the intensity of component on the number of groups may be found as according to formulas (3)-(5). One must approach aution those vibrations whose frequencies change y with changes in the number of groups, since this e associated with a disruption of the force field (and electro-optical parameters) of the equivalent groups elves.

s an example, we present the results of an investi- of the vibration intensities in the series of sub- s $(CH_3)_nSiCl_{4-n}$ (see Tables 1-3). The experimental ities have been taken by us from ref. 7. The me- al problem was solved by I. F. Kovalev, who kindly d to communicate his data.

Table 1. Si—C Bond Vibrations

Molecule	Symmetry type	Frequency (cm^{-1})	Intensity	
			Calc.	Expt.
$(CH_3)SiCl_3$	A . . .	764	1	1
$(CH_3)_2SiCl_2$	A_1 . . .	691	0.54	0.45
$(CH_3)_3SiCl$	A . . .	631	0.225	0.214

Table 2. Si—Cl Stretching Vibrations

Molecule	Symmetry type	Frequency (cm^{-1})	Intensity	
			Calc.	Expt.
$(CH_3)_2SiCl_2$	B_1 . . .	538	1	1
$(CH_3)SiCl_3$	E . . .	575	2.3	1.8

ll the computations were carried out according to la (5) for those vibrations relative to which the ful- nt of the necessary conditions could be assumed.

Table 3. Stretching Vibrations of the CH_3 Groups

Molecule	Symmetry type	Frequency (cm^{-1})	Intensity		
			Calc.	Intensity Calc. (total value)	Expt.
$(CH_3)SiCl_3$	A	2920	1	1	1
$(CH_3)_2SiCl_2$	A_1	2920	0.66	2	2
	B_1	2920	1.33		
$(CH_3)_3SiCl$	A	2905	0.33	3	3
	E	2905	2.66		
$(CH_3)_4Si$	F_2	2900	4	4	4.4

It is interesting to note that, in certain cases, the increase in the intensities of the bands under consideration with an increase in the number of CH_3 groups is a consequence of the superposition of different vibrations having identical frequencies. The theoretical investigation allows one to find the relative contributions of these vibrations to the total intensity which is observed experimentally.

In conclusion, I consider it my obligation to express my deep gratitude to I. F. Kovalev for providing all the necessary information on the solution of the mechanical problem.

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ON THE THEORY OF LINE INTENSITIES IN RAMAN SPECTRA
II. The Quantum Model (Taking Account of Anharmonicity and Deviation from the Condon Approximation

L. L. Krushinskii and P. P. Shorygin (pp. 151-160)

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The influence of deviations from the Condon approximation on the distribution of the contributions of the components of the vibrational structure in an excited electronic band to the polarizability matrix elements is investigated. The effect of anharmonicity of the ground and excited electronic states is calculated using perturbation theory. The relationship of the intensities of the Raman fundamental and first overtone, when far from resonance (the Placzek region of exciting frequencies), is determined.

In Part I of the present work[1] the quantum model of scattering molecules (the nuclear vibrations resemble harmonic oscillators) was investigated in the Condon approximation.

It was assumed that the dipole moment matrix element of the 0→e transition, formed from the electronic wave functions, does not depend on the internuclear distance, i.e., $M_{0e}(r) = \text{const}$.* However, experimental data on the energy distribution in the various components of electronic-vibrational spectra of diatomic molecules,[2-12] and also quantum mechanical calculations,[13-19] indicate that in the majority of cases this approximation is found to be too rough. The necessity for considering deviations from the Condon approximation [of the described functions $M_{0e}(r)$] also follows from results of measuring the dependence of Raman line intensities on the frequency of the exciting light when far from an absorption band.[20]

*All symbols are the same as those introduced in ref. 1.

In the present paper the quantum model with inclusion of the dependence $M_{0e} = M_{0e}(r)$ is examined. In addition the influence of the vibrational anharmonicity is accounted for by perturbation theory.

THE INFLUENCE OF DEVIATIONS FROM THE CONDON APPROXIMATION ON THE DISTRIBUTION OF THE SUBLEVEL CONTRIBUTIONS

The form of the functional dependence $M_{0e}(r)$ is really known for only a few electronic transitions in the simplest molecules (H_2^+, H_2, LiH).[14,16-19] In the remaining cases approximate calculations and analysis of the experimental data* permit one to approximate $M_{0e}(r)$ by some polynomial which can frequently be limited to a linear term

$$M_{0e}(r) = M_{0e}^0(1 + \gamma_i r). \qquad (1)$$

*Currently the r-centroids method[6,8] has received the broadest application for determining the form of the dependence $M_{0e}(r)$.

More seldom the quadratic approximation is required

$$M_{0e}(r) = M_{0e}^0(1 + \gamma_i r + \zeta r^2).$$

Equality (1) is approximate and satisfactorily gives the true nature of the dependence $M_{0e}(r)$ in a small interval of r values, including the equilibrium quantities r_0', r_0''. Obviously it is just this interval which is the most essential in calculating the respective integrals. Outside the indicated interval, calculation of the dependence $M_{0e}(r)$ in the form (1) leads to errors, which, however, are not large since the integrands rapidly diminish far from the equilibrium values of r.

The parameter η in formula (1) determines the degree of deviation from the Condon approximation. M_{0e}^0 represents a fictitious value of $M_{0e}(r)$, obtained by the extrapolation to $r = 0$.*

*It would be more descriptive to take account of deviations from the Condon approximation in the form

$$M_{0e}(q) = M^0(1 + \tilde{\gamma}_i q),$$

where $q = r - r_0''$ is the natural vibrational coordinate, and M^0 is the value of $M_{0e}(r)$ at the equilibrium nuclear position $r = r_0''$ (i.e., at $q = 0$). However, we will use representation (1) throughout since information in the literature on the dependence $M_{0e}(r)$ is given in just this form.

Formula (4) from Part I can be written in the following form:

$$a^{v_1'' v_2''} = \frac{1}{hc}(M_{0e}^0)^2 \cdot \sum_{v'} F(\nu; v') \cdot [(v', v_1'') + \gamma_i (v', rv_1'')]$$

$$\times [(v', v_2'') + \gamma_i (v', rv_2'')] = \frac{1}{hc}(M_{0e}^0)^2 \cdot \sum_{v'} F(\nu; v') \cdot B_{v'}^{v_1'' v_2''}.$$

Thus consideration of deviations from the Condon approximation is linked with calculations of integrals of the type (v', rv''), where

$$(v', rv'') = \int_0^\infty u_{v'}^{(e)}(r) \cdot r \cdot u_{v''}^{(0)}(r)\, dr.$$

In the future we will restrict ourselves to the case where the vibrational frequencies ω_0' and ω_0'', and accordingly also the forms of the potential curves of the ground and excited electronic states, are identical, keeping in mind the remarks made earlier concerning the general case. The calculational method of the similar integrals is given by Wagner.[21]

The scheme of this method, with a few changes, is as follows. Using the symbols of Part I one can write

$$(v', rv'') = r_0' \cdot (v', v'') + \frac{1}{a}\int_{-\infty}^{\infty} u_{v'}(X - K) \cdot (X - K) \cdot u_{v''}(X + K)\, d$$

Further, using the recursion formulas for Hermite ions,

$$\xi u_v(\xi) = \left(\frac{v+1}{2}\right)^{1/2} \cdot u_{v+1}(\xi) + \left(\frac{v}{2}\right)^{1/2} \cdot u_{v-1}(\xi)$$

btain

$$\frac{1}{\alpha}\int_{-\infty}^{\infty} u_{v'}(X-K)\cdot(X-K)\cdot u_{v''}(X+K)\,dX$$

$$= \frac{1}{\sqrt{\alpha}}\left[\left(\frac{v'+1}{2}\right)^{1/2}\cdot(v'+1,\ v'') + \left(\frac{v'}{2}\right)^{1/2}\cdot(v'-1,\ v'')\right].$$

The overlap integrals $(v'+1, v'')$ and $(v'-1, v'')$ are lated by formulas (9) from ref. 1. For definiteness ill take $v' \geqslant v''$. Then

$$\left(\frac{v'+1}{2}\right)^{1/2}\cdot(v'+1,\ v'') + \left(\frac{v'}{2}\right)^{1/2}\cdot(v'-1,\ v'')$$

$$= \frac{\sqrt{2}}{2}\cdot(-1)^{v'-v''-1}\cdot\left(\frac{v''!}{v'!}\right)^{1/2}\cdot\exp\left(-\frac{\alpha\Delta^2}{4}\right)\cdot\left(\sqrt{\frac{\alpha}{2}}\,\Delta\right)^{v'-v''-1}$$

$$\times\left[\frac{\alpha\Delta^2}{2}\cdot L_{v''+1}^{v'-v''+1}\left(\frac{\alpha\Delta^2}{2}\right) + v'\cdot L_{v''-1}^{v'-v''-1}\left(\frac{\alpha\Delta^2}{2}\right)\right].$$

For the following it is necessary to use the recursion ulas allowing one to decrease or increase the index e Laguerre polynomials (cf. ref. 21).

$$ZL_{n+\alpha+1}^{\alpha+1}(Z) = (n+\alpha+1)\cdot L_{n+\alpha}^{\alpha}(Z) - (n+1)\cdot L_{n+\alpha+1}^{\alpha}(Z);$$

$$+\alpha)\,L_{n+\alpha-1}^{\alpha-1}(Z) = (n+1)\cdot L_{n-\alpha+1}^{\alpha}(Z) - (n+1-Z)\cdot L_{n+\alpha}^{\alpha}(Z).$$

Accordingly,

$$\frac{1}{\sqrt{\alpha}}\left[\left(\frac{v'+1}{2}\right)^{1/2}\cdot(v'+1,\ v'') + \left(\frac{v'}{2}\right)^{1/2}\cdot(v'-1,\ v'')\right]$$

$$= (-1)^{v'-v''}\cdot\left(\frac{v''!}{v'!}\right)^{1/2}\cdot\exp\left(-\frac{\alpha\Delta^2}{4}\right)\cdot\left(\sqrt{\frac{\alpha}{2}}\,\Delta\right)^{v'-v''}$$

$$\frac{1}{\alpha\Delta}\left(v''-v'-\frac{\alpha\Delta^2}{2}\right)\cdot L_{v'}^{v'-v''}\left(\frac{\alpha\Delta^2}{2}\right) = \frac{1}{\alpha\Delta}\left(v''-v'-\frac{\alpha\Delta^2}{2}\right)\cdot(v',\ v'')$$

$$(v',\ rv'') = \left[\left(r_0'-\frac{\Delta}{2}\right)+\frac{1}{\alpha\Delta}(v''-v')\right]\cdot(v',\ v''), \qquad (4)$$

$'' \geqslant v''$.

In a similar manner one can show that

$$(v',\ rv'') = \left[\left(r_0''+\frac{\Delta}{2}\right)+\frac{1}{\alpha\Delta}(v''-v')\right]\cdot(v'',\ v'), \qquad (5)$$

$'' \leqslant v''$.

We introduce the symbol

$$\bar{r}_0 = \frac{1}{2}(r_0' + r_0''); \qquad (6)$$

t evident that $r_0' - (\Delta/2) = r_0'' + (\Delta/2) = \bar{r}_0$ and

$$(v',\ rv'') = \left[\bar{r}_0 + \frac{1}{\alpha\Delta}(v''-v')\right]\cdot(v',\ v'') \qquad (7)$$

any v' and u'' $(\Delta = r_0' - r_0'' \neq 0)$.

Using formulas (7) of the present work and (10) from 1 it is easy to calculate the contributions of the arate vibrational sublevels of an excited electronic e to the polarizability matrix elements of a molecule with account of the dependence $M_{0e}(r)$ in the form (1). Below are introduced results of the calculations for $B_v^{0v''}$ $(v'' = 0, 1, 2)$.*

*$B_v^{0v''}$ is the part of the contribution not depending on the frequency of the exciting light.

$$B_v^{00} = \frac{1}{v!}\cdot\left(\frac{\alpha\Delta^2}{2}\right)^v\cdot\exp\left(-\frac{\alpha\Delta^2}{2}\right)\cdot\left[(1+\eta\bar{r}_0) - \frac{\eta}{\alpha\Delta}v\right]^2; \qquad (8a)$$

$$B_v^{01} = \frac{1}{v!}\cdot\left(\frac{\alpha\Delta^2}{2}\right)^{v-1/2}\cdot\left(\frac{\alpha\Delta^2}{2}-v\right)\cdot\exp\left(-\frac{\alpha\Delta^2}{2}\right)$$

$$\cdot\left[(1+\eta\bar{r}_0)\left(1+\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right) - \frac{\eta}{\alpha\Delta}\left(2+2\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)v + \frac{\eta^2}{\alpha^2\Delta^2}v^2\right]; \qquad (8b)$$

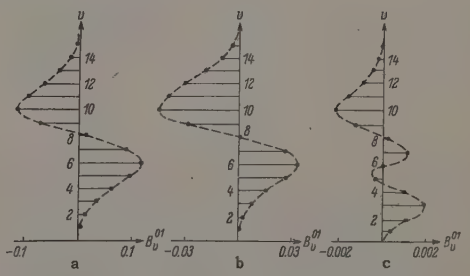
$$B_v^{02} = \frac{\sqrt{2}}{2}\cdot\frac{1}{v!}\left(\frac{\alpha\Delta^2}{2}\right)^{v-1}\cdot\left[\left(\frac{\alpha\Delta^2}{2}\right)^2 - 2v\cdot\frac{\alpha\Delta^2}{2} + v(v-1)\right]$$

$$\times\exp\left(-\frac{\alpha\Delta^2}{2}\right)\cdot\left[(1+\eta\bar{r}_0)\left(1+\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)\right.$$

$$\left. - \frac{2\eta}{\alpha\Delta}\left(1+\eta\bar{r}_0+\frac{\eta}{\alpha\Delta}\right)v + \frac{\eta^2}{\alpha^2\Delta^2}v^2\right]. \qquad (8c)$$

Analysis of formulas (8) leads to essentially differing results depending on whether the function $M_{0e}(r)$ retains or changes its sign in the interval where the representation (1) is valid.

In the first case, where the function $M_{0e}(r)$ does not change sign in the indicated interval, the basic features of the distribution of the contributions of the sublevels remain the same as in the Condon approximation (cf. the Figure, curves a and b).



A typical distribution form of the contributions of the vibrational sublevels of an excited electronic state to the magnitude of the polarizability matrix element a^{01}, determining the intensity of a first order Raman line. The curves are plotted for the following values of the parameters: $\alpha = 450 \times 10^{16}$ cm^{-2}; $\Delta = 0.2 \times 10^{-8}$ cm; $r_0' = 1.15 \times 10^{-8}$ cm; $\eta = 0$(a); $\eta = -0.70 \times 10^8$ cm^{-1} and $s_0 = -16$(b); $\eta = -0.84 \times 10^8$ cm^{-1} and $s = 5$(c).

1. The distribution of the contributions of the vibrational sublevels of the excited electronic state to a^{00} (for nonresonance excitation) is characterized by a single maximum, essentially coinciding with the Franck-Condon sublevel $v^* = E(\alpha\Delta^2/2)$. The contributions of all of the sublevels are positive.

2. The distribution of the contributions of the sublevels to a^{01} is characterized by one sublevel making a zero (or close to zero) contribution (this is exactly the Franck-Condon sublevel) and by two sublevels making extreme contributions [the distance between them is determined by the formula $(v_1 - v_2)q^{01} = \Delta$]. When outside the resonance region one can approximately replace the

totality of the vibrational structure components of the actual excited electronic level by two conditional effective sublevels, summing respectively the contributions of the group of upper and lower (with respect to v^*) sublevels, making contributions of opposite signs. A new feature, on taking account of the dependence $M_{0e}(r)$, is that the distribution of the contributions possesses a significant asymmetry with respect to v^*, leading to a breakdown of the summed compensation of the contributions even in the case where the frequency factor can be considered constant for all v.

3. The distribution of the contributions of the sublevels to a^{02} is characterized by two "nonessential" (i.e., making contributions close to zero) sublevels and by three sublevels making extreme contributions. However, here also consideration of deviations from the Condon approximation produces a breakdown of the summed compensation of the quantities B_v^{02}.

In the second case, in which the function $M_{0e}(r)$ changes sign in the interval for which representation (1) is valid, the distribution of the contributions by comparison with that occurring in the Condon approximation undergoes more or less significant changes (there appear additional "nonessential" sublevels and sublevels making extreme contributions). The features in this instance are linked with the splitting of the absorption band produced in this case.

Indeed, if v_0 is the sublevel to which the zero intensity component in the absorption spectrum corresponds, then according to Jarmain[8]

$$(v_0,\ M_{0e}(r)\,0) = M_{0e}(\bar{r}_{v_0,0}) \cdot (v_0,\ 0),$$

but, since $(v_0, 0) \neq 0$, $M_{0e}(r_{v_{0,0}}) = 0$, i.e., the curve $M_{0e}(r)$ intersects the abscissa axis at the point $r = r_{v_{00}}$.

From (8a) it follows that the sublevel $v_0 = E(s_0)$, defined by the formula

$$s_0 = \frac{a\Delta}{\eta}\left(1 + \eta r_0'' + \frac{\eta_i \Delta}{2}\right) \cong \frac{a\Delta}{\eta}\left(1 + \eta r_0''\right), \qquad (9)$$

makes a zero contribution to the intensity distribution with respect to the vibrational structure components of the electronic-vibrational band.*

*It is evident that (9) has a physical meaning only for those values of the parameters appearing in it which guarantee $s_0 > 0$. In practice, moreover, the values of s_0 should not be very large in order that the corresponding sublevel fall in the zone, effective for absorption.

1. The distribution of the contributions of the sublevels to a^{00}, duplicating for nonresonance excitation the structure of the absorption band, is characterized by the appearance of a "nonessential" (i.e., making a zero contribution) sublevel $v_0 = E(s_0)$ and of two sublevels giving maximum contributions. The latter are determined by the equation*

*Equation (10) has a singularity at the point $s = s_0$. For $s_0 > 0$ the curve $\Phi_0(s)$ (defined along the positive semiaxis s) will have two branches, asymptotically approaching the straight line $s = s_0$. This also guarantees obtaining two solutions. For $s < 0$ (this corresponds physically to the absence of band splitting) $\Phi_0(s) \cong \Psi(s)$ and (10) transforms into Eq. (14) of ref. 1.

$$\Phi_0(s) \equiv \Psi(s) + \frac{2\eta}{a\Delta} \cdot \frac{1}{\left(1 + \eta r_0'' + \frac{\eta_i \Delta}{2}\right) - \frac{\eta}{a\Delta} s} = \ln \frac{a\Delta^2}{2}. \qquad (10)$$

2. It is not hard to show that, on splitting of the absorption band, produced by $M_{0e}(r)$ going to zero close to the equilibrium values of r, zero (close to zero) contributions to a^{01} are made by three sublevels, one of which coincides with the Franck-Condon v^*, and the numbers of the other two are determined by the formulas

$$\left.\begin{aligned} v_1 &= E(s_1); \quad s_1 = \frac{a\Delta}{\eta_i}\left(1 + \eta r_0'' + \frac{\eta\Delta}{2}\right) = s_0; \\ v_2 &= E(s_2); \quad s_2 = \frac{a\Delta}{\eta}\left(1 + \eta r_0'' + \frac{\eta\Delta}{2} + \frac{\eta}{a\Delta}\right) = s_0 + 1. \end{aligned}\right\} \qquad (1$$

Moreover the number of extrema in the distributio of B_v^{01} can reach four. Thus in the case examined the scheme of two effective sublevels introduced in ref. 1 appears inapplicable (cf. the Figure, curve b).

An analogous, but much more complex picture occurs also in examining a^{02}.

We have based our arguments on the assumption that the dependence $M_{0e}(r)$ can be approximated by expression (1) in some interval of r. It is easy to see, however, that this assumption was required mainly to simplify the calculations, but the results obtained have broader character. The basic results (particularly concerning the rule of the splitting of the absorption band) are conserved also for any monotonic representation of $M_{0e}(r)$.

It is quite important that taking account of deviations from the Condon approximation [in any form, independently of the possibility of a sign change of $M_{0e}(r)$] leads to a breakdown of the summed compensation of th A_v^{01} and A_v^{02} contributions, even if differences of the frequency factors of the separate sublevels (cf. the Figure are neglected. If one starts from expression (1) for the dependence $M_{0e}(r)$ one can without difficulty obtain the following formulas in the harmonic oscillator approxim tion:

$$\left.\begin{aligned} \sum_{v=0}^{\infty} B_v^{00} &= 1 + 2\eta_i r_0'' + \eta_i^2\left(r_0'' + \frac{1}{2a}\right); \\ \sum_{v=0}^{\infty} B_v^{01} &= \frac{2\eta}{\sqrt{2a}}\left(1 + \eta_i r_0''\right); \\ \sum_{v=0}^{\infty} B_v^{02} &= \sqrt{2} \cdot \frac{1}{2a} \cdot \eta_i^2. \end{aligned}\right\} \qquad (1$$

Formulas (12) permit the evaluation of the intensit ratio of the Raman fundamental and first overtone for excitation in the Placzek region.*

*As is known,[22] the region of applicability of the Placze theory is characterized by a separation of the frequenc of the exciting light from an absorption band sufficientl large that the differences of the frequency factors of the separate sublevels can be neglected.

Using formulas (2), (12), and also (5) from ref. 1 a remembering that the zero point vibrational amplitude the nuclei is

$$q^{01} = \frac{1}{\sqrt{2a}} = \left(\frac{\hbar}{8\pi^2 c \mu \omega_0''}\right)^{1/2},$$

we find that in the indicated region

$$a^{01} = \frac{2}{\hbar c} \cdot \frac{\nu_e}{\nu_e^2 - \nu^2} \cdot (M_{0e}^0)^2 \cdot 2\eta\left(1 + \eta r_0''\right) \cdot \left(\frac{\hbar}{8\pi^2 c \mu \omega_0''}\right)^{1/2} \qquad (1$$

(ν_e is the frequency of the absorption band maximum) a

$$a^{02}=\frac{2}{hc}\cdot\frac{\nu_e}{\nu_e^2-\nu^2}\cdot(M^0_{0e})^2\cdot\sqrt{2}\,(\eta^2+2\zeta)\cdot\frac{h}{8\pi^2c\mu\omega_0''} \qquad (14)$$

rmula (14) we have used the more accurate expres-
$M_{0e}(r)=M^0_{0e}(1+\eta r+\zeta r^2)$, since the moduli of the
ties η and ζ are generally speaking of the same
].

n the Placzek region of exciting frequencies the
ction of the Raman fundamental and overtone is due
same cause—deviations from the Condon approxi-
n.* Formulas (13) and (14) define an identical and

ideration of the mechanical anharmonicity changes
agnitudes of a^{01} and a^{02}, but by itself mechanical
monicity cannot lead to production of an overtone.

aratively slow growth of the intensities of first and
d order lines on an increase of the frequency of the
ng light. The ratio of the intensities of the funda-
l and first overtone, for the same frequency, ν, of
cident light, can be found from the following for-

$$\frac{I_2}{I_1}\sim\left(\frac{a^{02}}{a^{01}}\right)=\left[\frac{\sqrt{2}\,(\eta^2+2\zeta)}{2\eta\cdot(1+\eta r_0'')}\right]^2\cdot\frac{h}{8\pi^2c\mu\omega_0''}\cdot \qquad (15)$$
$(\nu\ll\nu_e)$.

For typical values of the parameters in (15) we ob-
$I_2/I_1\sim10^{-3}$, which is not in conflict with available
imental estimates.[23,24] In the Placzek approxima-
he ratio I_2/I_1 is completely independent of ν and,
ntrast with the case of the applicability of the Con-
pproximation, it is only slightly sensitive to a change

SIDERATION OF THE MECHANICAL ANHARMONICITY

Investigation of the question concerning the influ-
of the nuclear vibrational anharmonicity on the dif-
t order Raman spectra is of significant interest.
difficulties in the solution of this problem are con-
d with the calculation of the overlap integrals in the
e oscillator approximation. Even in the simplest
s quite involved expressions are obtained which are
menable to analysis.[25]

Many qualitative results can be obtained for a small
monicity by using the known results for the anhar-
c oscillator and considering the nonlinear terms in
xpression for the potential curve U(r) as a perturba-

Having written the perturbation operator in the form

$$\hat H=\hat H^{(1)}+\hat H^{(2)}=l(r-r_0)^3+m(r-r_0)^4, \qquad (16)$$

e $l=(1/3!)(\partial^3U/\partial r^3)_{r=r_0}$ and $m=(1/4!)(\partial^4U/\partial r^4)_{r=r_0}$
the anharmonicity constants, r_0 is the equilibrium
e of the internuclear distance, one can show[26] that the
e functions of the anharmonic oscillator

$$\left(U(r)=\frac{1}{2}k(r-r_0)^2+l(r-r_0)^3+m(r-r_0)^4\right)$$

expressed in terms of harmonic oscillator wave
tions in the following manner*

$u^{(0)}_v(r)$ is a harmonic oscillator wave function (zero
roximation).

$$u_v(r)\simeq u_v^{(0)}(r)+\frac{l\beta^3}{hc\omega_0}\Big[\frac{1}{3}\left((v-2)(v-1)v\right)^{1/2}\cdot u^{(0)}_{v-3}(r)+3v^{3/2}\cdot u^{(0)}_{v-1}(r)$$
$$-3(v+1)^{3/2}u^{(0)}_{v+1}(r)-\frac{1}{3}\left((v+1)(v+2)(v+3)\right)^{1/2}u^{(0)}_{v+3}(r)\Big]$$
$$+\frac{m\beta^4}{hc\omega_0}\Big[\frac{1}{4}\left((v-3)(v-2)(v-1)v\right)^{1/2}\cdot u^{(0)}_{v-4}(r)$$
$$+2\left((v-1)\left(v-\frac{1}{2}\right)^2v\right)^{1/2}\cdot u^{(0)}_{v-2}(r)$$
$$-2\left((v+1)\left(v+\frac{3}{2}\right)^2\cdot v\right)^{1/2}u^{(0)}_{v+2}(r)$$
$$-\frac{1}{4}\left((v+1)(v+2)(v+3)(v+4)\right)^{1/2}\cdot u^{(0)}_{v+4}(r)\Big];\quad \beta=q^{01}. \qquad (17)$$

We will restrict ourselves to an examination of the wave functions obtained on application of the operator $\hat H^{(1)}$ $l(r-r_0)$.[3]* Moreover, for simplicity we will examine the

*It is not hard to show that consideration of the perturbation $\hat H^{(2)}=m(r-r_0)^4$ leads to the same conclusions; however, it is expressed considerably less clearly. This is related with the fact that the ratio of the corrections in anharmonicity in (17), described by the operators $\hat H^{(1)}$ and $\hat H^{(2)}$, have an order $m\beta/|l|\sim10^{-2}$.

case where the forms of the potential curves of the ground and excited states are identical. Below are introduced formulas for the $B_v^{0v''}$, describing for nonresonance excitation the distribution of the sublevel contributions to the polarizability matrix elements:

$$B_v^{00}=\frac{1}{v!}\exp(-x^2)\,x^{2v}\left[1+\lambda v\left(x-(v-1)x^{-1}\right)\right]; \qquad (18a)$$

$$B_v^{01}=\frac{1}{v!}\exp(-x^2)\,x^{2v-1}\left\{(x^2-v)+\lambda\left[2x^{-1}\cdot v^3\right.\right.$$
$$\left.\left.-4(x+x^{-1})v^2+2(x^3+x+x^{-1})v-x^3\right]\right\}; \qquad (18b)$$

$$B_v^{02}=\frac{\sqrt{2}}{2}\frac{1}{v!}\exp(-x^2)\,x^{2v-2}\cdot\left\{(v^2-(2x^2+1)v+x^4)\right.$$
$$-\lambda\left[2x^{-1}v^4-2(3x+4x^{-1})v^3+6(x^3+2x+2x^{-1})v^2\right.$$
$$\left.\left.-2(x^5+3x^3+3x+3x^{-1})v+2x^3(x^2-1)\right]\right\}. \qquad (18c)$$

Here $\lambda=4l\beta^3/hc\omega_0$ ($l<0$ always), $x=\sqrt{\alpha/2\Delta}$. Strictly speaking formulas (18) can be used only in the case of small anharmonicity. However they can be successfully applied to obtain some qualitative conclusions. We first note that consideration of anharmonicity leads to a decrease of the absolute values of the quantities $B_v^{0v''}$ ($v''=0,1,2$). Further, even for values of $|l|$ which are not large (with fixed Δ) a substantial shift (in the direction of larger v) of the numbers of the sublevels making zero contributions to a^{01} and a^{02} is produced. The number of extrema in the distributions of the sublevels contributions remains unchanged, but their location is altered. Thus the number of the sublevel making the maximum contribution to a^{00} for nonresonance excitations can be found from the expression

$$\Psi(s)=\frac{2\lambda(2x^{-1}s+(x+x^{-1}))}{1+\lambda x^{-1}s+\lambda(x+x^{-1})s^2}=\ln x^2. \qquad (19)$$

For example, with $x=3$ and $l=-20\times10^{13}$ cm^{-3} erg,* $v_{max}=13$, while for harmonic vibrations with $x=$

*In addition $\omega_0=2000$ cm^{-1}, $\beta=0.03\times10^{-8}$ cm.

3 we would obtain $v^*=9$. The presence of anharmoni-

city naturally leads to the necessity for examining a significantly larger number of sublevels.

It is expedient to evaluate separately, albeit only qualitatively, the role of anharmonicity of the ground and excited electronic states.

The nuclear vibrational anharmonicity in the excited electronic state is the more substantial in the case where differences of the frequency factors of the separate sublevels (excitation close to and in the resonance region) play a significant role. Its influence manifests itself in the appearance of a convergence of the sublevels (significantly changing the frequency factors), as well as in a change of the form of the potential curve (affecting the magnitudes of the contributions and the distribution of the sublevels making the extreme contributions). On the other hand, in the Placzek region anharmonicity of the excited state can be ignored.

Vibrational anharmonicity in the ground electronic state introduces only small corrections in the examination of scattering in the resonance region (since, for low v, the wave functions of an anharmonic oscillator differ little from those of a harmonic oscillator). It is much more essential to consider anharmonicity for the ground electronic state in the Placzek region, particularly in the overtone case. Considering anharmonicity formula (14) can be written in the following form

$$a^{02} = \frac{2}{hc} \cdot \frac{\nu_e}{\nu_e^2 - \nu^2} \cdot (M_{0e}^0)^2 \cdot [2\eta r^{02} + (\eta^2 + 2\zeta) \cdot (r^2)^{02}]. \quad (20)$$

Here $r^{02} \neq 0$, and the first term in the square brackets is commensurate in absolute magnitude with the second. However, the possibility is not excluded that consideration of the mechanical anharmonicity can produce some weakening of the overtone line intensity [if the signs of the quantities η and $(\eta^2 + 2\zeta)$ are opposite]. As a rule the order of magnitude is not changed on taking account of anharmonicity in the Placzek region.

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HE INTENSITY OF RAMAN BANDS AND THE CHARACTER OF THE CHEMICAL BOND

Ya. S. Bobovich (pp. 161-168)

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The intensity of first order Raman bands in the spectra of 36 molecules and anions, and also in the spectra of a series of complex glasses, have been measured. The results are compared with the electronegativity difference of the respective atoms, acting as a measure of the polar character of the bond. In the majority of cases there is a qualitative correlation between the compared quantities. It is shown that the state of the valence orbitals of the atoms examined is reflected simply in the Raman spectra.

RODUCTION

For a long time chemists have used the idea of elec-egativity of the atoms in a molecule for the inter-ation of a variety of molecular properties. Simply use we are talking here about atoms in molecules, not about isolated atoms, an accurate definition of property (without even considering its measurement) esents a hard problem.

Examining the diatomic molecule AB with a simple , Mulliken quantitatively characterizes the electro-tivity x of, for example, atom A by the average of irst ionization potential I_A and its first electron af-y E_A.[1] If the atoms are characterized by variable nce, then still more electrons are needed to realize igher states. The higher ionization potentials and tron affinities corresponding to this should be intro-d into the examination. These refer to physical esses about which, in the general case, little is n. Nonetheless, it is clear that this should be re-ed in the quantity $(I_A + E_A)/2$. It means that the tronegativity x of an atom will depend on its valence. nical experience shows without doubt that the greatest tallicness," i.e., the lowest electronegativity, al-s corresponds to the lowest valence state of an atom.

Of course, this is not uninfluenced by the particular tron which participates in the bond formation. This lear in the example of s-electrons. Since the separa-of an s-electron from an atom generally is ac-panied by a relatively large expenditure of energy, articipation in the formation of a bond must inevit-increase the electronegativity of the atom. Accord-y, there will correspond to an increase in the s-es' share of the hybrid bonding orbital a higher atomic tronegativity. This view has been expressed in the ature and has actually been confirmed by quantum hanical calculation.[2,3]

Thus, strictly speaking, it is more correct to re-the electronegativity not to the atoms, but to their nce clouds. In other words one should attribute not , but a whole set of x values, to each atom depending ts valence state.

In the course of many years a series of methods for rmining electronegativities has been proposed. Elec-negativity scales have been created. In some of them tronegativity is considered as an invariable property he atom, in others the specifics of the valence states accounted for to different degrees. Among these the le which has received the widest acceptance is un-btedly Pauling's,[4] based on the use of the thermochem-l properties of the molecules formed from the atoms ypical valence states. It should be noted, however, that Pauling's scale has been repeatedly exposed to criticism (cf., e.g., ref. 5 and 6, and also ref. 7). Some difficulties have evidently been successfully removed by the authors of ref. 8 who have constructed a modified scale for 54 elements. In many cases the old values have been substantially improved. In the following we will use the values found to ref. 8 to evaluate the character of a chemical bond by the electronegativity difference.

The assertion that the electronegativity of an element depends on its valence state has found confirmation in the calculations of Haissinsky.[9] It was found that the highest electronegativity of an atom always corresponds to its highest valence. This conclusion will also be heeded in the discussion of the results.

I. A SPECTROSCOPIC CRITERION OF BOND TYPE

The London criterion[10,11] agrees well with the experimental facts and with a general physical representation of the stability of different energetic states. Let A and B be two atoms forming a molecule. If the bond between them is known to be ionic the potential curves of the normal (ionic) and lowest of the excited (atomic) states will be situated as shown in Fig. 1a. The distance between the asymptotes of the two curves is equal to the difference of the ionization potential I_A of the first and the electron affinity E_B of the second atom. Accordingly, with an increase of the bond ionic character and asymptotes should approach and merge in the limit. To this there corresponds a shift of the intersection point of the hyperbolic branch of the lower curve with the asymptote of the upper in the direction of larger values of the internuclear distances, significantly exceeding the equilibrium values.

Let us now examine a case known to be an atomic bond. Its corresponding potential curves are shown in Fig. 1b. Here there already corresponds to the excited segment of the asymptote of the atomic curve an internuclear distance commensurate with the equilibrium value, and increasing on the approach of the two asymptotes. Merging of the asymptotes obviously denotes a transition to a purely ionic bond.

Thus the magnitude of the examined segment of the asymptote of the atomic potential curve, being in direct dependence on the difference $I_A - I_B$, can, according to London, serve as a measure of the chemical bond type.[10,11]

It is not hard to show the existence of a parallel behavior of the quantities $I_A - E_B$ and $I_A + E_A$. The latter sum, according to Mulliken, as noted earlier, characterizes with an accuracy to a constant factor the relative electronegativity of atom A. Therefore, the merging of

the asymptotes denotes a decrease of the electronegativity of one atom in comparison with the other, i.e., an increase of the ionicity of the bond. Accordingly, the application of the London and Mulliken criteria to an estimate of bond type leads to identical results.

Theoretical investigations of the relation between the Raman bond intensity and the chemical bond type represent an extraordinarily complex problem. On applying the London criterion one can only make a few comments on this question in the simplest of cases.

As is known the production of Raman scattering is due to a periodic change of the molecular polarizability in the course of its nuclear vibrations. In the harmonic approximation of semiclassical theory the first order Stokes Raman band intensity can be expressed in the following manner:

$$I \sim \frac{(\nu_0 - \nu_v)^4}{\mu \cdot \nu_v} \cdot \frac{1}{1 - \exp\left(-\frac{h\nu_v}{kT}\right)} \frac{1+\rho}{6-7\rho} \left(\frac{\partial \alpha}{\partial Q}\right)_0^2, \quad (1)$$

where ν_0 and ν_v are the frequencies of the exciting line and vibrational bond respectively, μ is the reduced mass of the vibrating nuclei, $\partial\alpha/\partial Q$ is the polarizability derivative with respect to the normal coordinate, ρ is the degree of depolarization of the vibrational bond, h and k are the Planck and Boltzmann constants respectively, and T is the absolute temperature. An investigation of the chemical bond properties requires a knowledge of the quantities $\partial\alpha/\partial q$ where q is the natural coordinate (change of the bond length). In the following, a transition from one coordinate to the other will be realized for the simplest case—for the completely symmetric vibrations of a few molecules. Thus, for example, this leads for tetrahedral molecules to the introduction of a factor, equal to 2, into (1).

In accordance with Vol'kenshtein[12] the derivative $\partial\alpha/\partial q$ is related to a series of molecular quantities in the following way:

$$\frac{\partial \alpha}{\partial q} \cong -\frac{1}{h} \sum_e \frac{2(\nu_e^2 + \nu_0^2)}{(\nu_e^2 - \nu_0^2)^2} \left(\frac{\partial \nu_e}{\partial q}\right)_0 |P_{0e}|_0^2. \quad (2)$$

Here ν_e is the frequency of the electronic-vibrational band, and P_{0e} is a matrix element component of the dipole moment of the purely electronic transition. In the general case the summation extends over all the electronic-vibrational states.

With formula (2) all of the difficulties of solving the problem posed immediately disappear. It is not hard to show that the quantity $(\partial\nu_e/\partial q)_0$ characterizes the slope of the upper potential curve at its point of intersection with a vertical arrow depicting the optical transition from the minimum of the lower curve. Accordingly, the first order Raman band intensity should depend only on the properties of the excited states. At the same time the distance between the asymptotes of the curves and, concurrently, according to the London criterion, also the bond type, can be determined by the form of the lower curve. Further, the London criterion has a clear physical meaning in the case where the upper curve refers to nearly ionic (or atomic) states, and the derivative $\partial\alpha/\partial q$, according to formula (2), generally speaking, depends on the totality of excited electronic states. Finally one must also keep in mind the influence on the derivative $\partial\alpha/\partial q$ of the factor P_{0e}, which does not have an obvious correlation with the character of the chemical bond.

In the simplest case for the examination of the Raman band let only one transition from the lower, ionic, to the upper, atomic, state be essential (Fig. 1a). Then, using the Morse approximation, one can show that $(\partial\nu_e/\partial q)_0 \cong -(2D'a'^2q')/h$, where D' and a' are constants of the Morse function (the first of them has the meaning of the dissociation energy) and q' is the change of the equilibrium internuclear distance for the electronic excitation.[12] It is known from experience that the upper state in typically ionic molecules has a low stability, by virtue of which they are characterized mainly by a continuous absorption. Accordingly, on an increase of the bond ionicity the upper curve of Fig. 1a should become less stable, rising higher (shown by the dashed curve). Since then the magnitude of the product $D'a'^2$ necessarily decreases and the value of the frequency ν_e increases, the derivative $\partial\alpha/\partial q$ will decrease (this is also subject to the influence of the factor P_{0e}), and together with it also the intensity of the corresponding Raman band. Experience shows that the absorption intensity, i.e., the quantity P_{0e}, generally acts in the same direction. It is not hard to see that the influence of a possible change of q' compensates to a known degree the change of ν_e arising from it. Thus, in the end the magnitude of the derivative $\partial\alpha/\partial q$ should serve as a measure of the bond polarizability in the case examined.

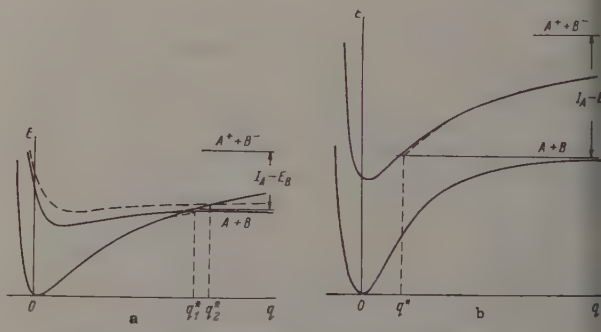

Fig. 1. The potential curves of the states corresponding to photodissociation into atoms (a) and ions (b). On an increase of the bond ionic character the upper solid curve in case (a) transforms into the broken one. The segments of the asymptote of the atomic curve, cut off by the extended hyperbolic branch of the ionic curve, are denoted by the symbol q*.

It has already been remarked above that it is difficu to solve the posed problem in the general form. Therefore, in the present work we have made an attempt to establish experimentally the possibilities of applying data on the Raman intensities as criteria of the chemical bon type. For this purpose a wide range of substances was investigated. The most characteristic results are given below.

The spectra of all of the substances, with the exception of one (the CrO_4^{-6} anion), were recorded photoelectrically using a DFS-12 instrument. To account for the influence of the internal field of the substance on the ban intensity we prepared solutions and mixtures with approximately identical values of the refractive index or used the internal standard method.[13,14] In all cases the integrated band intensity was measured.

CHLORIDES OF SOME ELEMENTS OF THE SECOND, FOURTH, AND FIFTH GROUPS OF THE PERIODIC TABLE; OXYGEN-CONTAINING ANIONS

In Table 1 are presented the results of measuring intensity of the completely symmetric vibration and calculating the derivative for a series of chlorides. data relating to the oxygen-containing anions is n in Table 2. In a few cases where information on the rational form is absent the values of the derivatives approximate. A comparison with the magnitudes of electronegativity differences of the atoms forming anion has a doubly approximate meaning, since the ms are, as a rule, located in valence states different m those on which the Pauling scale is based.

As is seen from the data of the two tables there is, n overwhelming majority of cases within the limits ach group of elements of the periodic system, a reable qualitative correlation between the measured band intensity and the calculated values of the derivatives $\partial\alpha/\partial q$, on the one hand, and the bond polarity, as a measure of which is chosen the electronegativity difference of the corresponding atoms, on the other. Heeding the reservation regarding the valence of the elements in the group of anions, one can say that only the CCl_4 molecule forms an exception. The impression is created that carbon is less electronegative than the majority of the other group IV elements. But this is erroneous. There are no doubts of the strongly covalent character of the C—Cl bond. This contradiction arises from the inadequacy of the spectroscopic criterion, and will be clarified in detail in another communication.

The correlation between the Raman band intensity the bond character evidently does not depend on the state of aggregation of the substance. This follows from the fact established earlier that the spectral bands of glassy GeO_2 are substantially more intense than the SiO_2 bands,[16] and this means their behavior is the same as in the $GeCl_4$ and $SiCl_4$ molecules respectively. In the present study the same conclusion is proven by a comparative investigation of complex glasses containing magnesium, zinc, cadmium, titanium, zirconium, bismuth, and a few other elements.

Thus Raman band intensities are actually a rather universal criterion of bond type.

Table 1. Comparison of the Raman Band Intensity of the Completely Symmetric Vibrations and the Values of the Bond Polarizability Derivatives with the Magnitude of the Electronegativity Difference $x_{El} - x_{Cl}$ for a Few Chlorides

No.	Molecule	Frequency (in cm^{-1}) and intensity (on a single scale) of the spectral bands	Degree of depolarization of the bands	$\left(\frac{\partial\alpha}{\partial q}\right)_{av}$ (A^2)	$x_{El} - x_{Cl}$
1	$BeCl_2$ . . .	520 (0.4)	0. 1	0.27*	1.49
2	$MgCl_2$ . . .	200 (1.5)	≈0.05	0.26	1.38
3	$ZnCl_2$ . . .	280 (11)	0.02	0.91	0.98
4	$CdCl_2$ . . .	230 (18)	0.03	1.1	0.78
5	CCl_4 . . .	459 (52)	0.02	2.00**	0.58
6	$SiCl_4$ . . .	424 (58.8)	0.08	1.99	1.25
7	$GeCl_4$ . . .	396 (156)	0.05	3.12	1.13
8	$SnCl_4$ . . .	366 (291)	0.05	4.04	0.68
9	$TiCl_4$ . . .	386 (483.6)	0.05	5.4	0.93
10	$ZrCl_4$ . . .	315 (52)	Partially polarized	—	1.05
11	PCl_3 . . .	510 (82)	0.14	—	0.96
12	$SbCl_3$ . . .	360 (213)	—	—	0.87
13	$BiCl_3$ . . .	288 (246)	—	—	—

*The value of the derivative $\partial\alpha/\partial q$ for $BeCl_2$, as also for the other molecules of the second group elements, is calculated assuming their structure is linear. However, this is contradicted by the very low values of the degrees of depolarization of the bands. It is possible that these substances in solution form complex ions.

**The absolute value of the derivative according to the calculation in ref. 15 (cf. also ref. 17).

Table 2. Comparison of the Raman Band Intensity of the Completely Symmetric Vibrations and the Values of the Bond Polarizability Derivatives with the Magnitude of the Electronegativity Difference $x_{El} - x_O$ for Oxygen-Containing Anions

No.	Anion	Frequency (in cm^{-1}) and intensity (on a single scale) of the spectral bands	Degree of depolarization of the bands	$\left(\frac{\partial\alpha}{\partial q}\right)$ av. (A^2)	$x_{El} - x_o$
1	CO_3^{-2} . . .	1060 (10)	0.11	1.05	0.88
2	NO_3^- . . .	1050 (29)	0.16	1.70	0.47
3	PO_4^{-3} . . .	935 (10.9)	0.05	0.97	1.26
4	AsO_4^{-3} . . .	840 (33.3)	0.12	1.44	1.48
5	SO_4^{-2} . . .	980 (22)	0.03	1.33	—
6	CrO_4^{-6} . . .	856 (120—140)*	—	3.3	1.16
7	MoO_4^{-6} . .	900 (100)	0.04	2.86	0.89
8	WO_4^{-6} . . .	925 (65)	0.09	2.30	1.07

*The intensity is estimated from the degree of darkening of a photographic plate. It is possible that the measured intensity does not refer completely correctly to the bond state in view of the redness of the anion (the resonance phenomenon).

III. INFLUENCE OF THE ATOMIC VALENCE

It has been shown by measurements that the band intensity per bond of the completely symmetric vibration of stannic chloride, dissolved in alcohol, is in a ratio of 28.4 : 17 to the corresponding quantity of stannous chloride. This obviously arises from a less polar character of the bond in the first case, i.e., from a higher electronegativity of the four-valent tin atom. In the arrangement of the normal Sn atom there are two 5p valence electrons. Its excitation consists of an unpairing of the 5s electrons and a transposition of one of them to a vacant p orbital. The subsequent formation of a hybrid sp^3 orbital requires some s-state contribution, and this also leads to an increase of the tin atom electronegativity, fixed by the spectroscopic method.

The spectral band intensity coefficient of phosphorous pentachloride increases substantially (approximately five times) in comparison with the trichloride. There is no doubt that in this instance the phosphorous atom undergoes a transition from the initial p^3 state into excited sp^3d or s^2p^3 states with the participation of the s-orbitals. The anions of six- and four-valent sulfur behave in an analogous manner. The corresponding intensity coefficients of the completely symmetric vibrations are in the ratio 5.5 : 4.0. This is understandable if we consider that six-valent sulfur acquires some additional s-state contribution.

The behavior of anions containing seven- and five-valent halogens is very interesting. It is found that the intensity coefficients of the completely symmetric vibrations grow and do not decrease on going from the ClO_3^- anion to the BrO_3^- and IO_3^- anions (28 : 31 : 50). This means that five-valent iodine, let alone bromine and chlorine, is more electronegative than oxygen. Judging by the data of ref. 17, the intensity coefficient for the analogous vibration of the ClO_4^- anion, in which the chlorine has a valence of seven, equals 9.0 in the same units, i.e., is much smaller in magnitude than the coefficient of the anion with five-valent chlorine. This obviously at-

tests to a further increase of the chlorine electronegativity. All of the facts noted above also yield to an interpretation from the viewpoint of changes in the hybrid valence orbitals.*

*However, it is hard to estimate the possible influence of the d-orbitals.

Thus, the generally accepted idea of chemists concerning the increase of "metallicness" of an atom in its lowest valence state finds a direct reflection in the Raman spectra.

IV. INFLUENCE OF THE CHARACTER OF THE BONDING ORBITALS WITH AN UNCHANGED ATOMIC VALENCE

The largest differences in electronegativity, discovered for one atom with unchanged valence, are inherent in carbon, whose valence states are characterized by one of three possible hybridization types—sp^3, sp^2, and sp. This is immediately proven by the increase of acidity in the series methane, ethylene, acteylene.[3] On the basis of the above exposition differences in the hybridization types should be reflected in the intensity of the vibration of the bond joining carbon with the other atom, hydrogen, for example. To verify this circumstance we made a comparitive investigation of the stretching vibrations of hydrogen, bonded to methyl, ethylenic, and acetylenic carbons. In this we consciously chose those molecules in which different bonds of like kind were present together. The summed intensity of the complex bands in the region of the C—H stretching vibrations, related to one CH group, served as a measure of the intensity coefficient. Thus the influence on the measured quantity of the form of the corresponding vibration, as well as the intensity of the actual absorption bands, was excluded.

The results of the measurements, averaged for a series of molecules, are shown graphically in Fig. 2. A distinct dependence of the intensity coefficient of the examined vibration on the carbon hybrid orbital type is seen. As one would expect the largest intensity corresponds to the sp^3 state and the smallest to the sp state, in complete agreement with other investigations.[18] Our attention is attracted to the strict proportionality between the measured quantity and the percentage share of the s-state orbitals. This latter fact needs further interpretation. One can hence conclude that variations of the character of the bonding orbitals for an unchanged atomic valence are revealed in the Raman spectra.

For a long time the question of the orientation of the C—H bond dipole moment has been discussed in the literature. A theoretical calculation made by Coulson[19] shows that the positive end of the dipole is directed towards the carbon. The shift of the band intensity of the CH bond vibration in its dependence on the hybridization type contradicts this viewpoint. It proves the opposite orientation of the dipole, at least for the molecules investigated.

Thus, an investigation of the intensities in the Raman spectra can give valuable information on the nature of the chemical bond in the majority of cases. In addition, it is realized that data on the intensities, characterizing not only the limiting but also the intermediate states of the bonds, are applicable to and can be equally easily obtained for complex as well as simple molecules, independent of the state of aggregation of the substance.

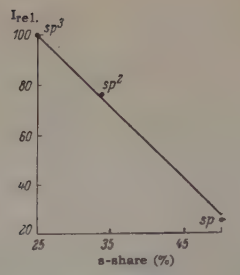

Fig. 2. Graph of the dependence of the intensity coefficient of the Raman band corresponding to the stretching of CH bonds on the share of s-states in the bonding orbitals. The points are obtained by averaging data for crotyl bromide, allyl and propargyl alcohols, diisobutylene, butylacetylene, toluene, and the three isomeric xylenes.

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AN INVESTIGATION OF THE RAMAN INDICATRIX

I. I. Kondilenko, P. A. Korotkov, and V. L. Strizhevskii (pp. 169-174)

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The Raman indicatrix for 16 normal vibrations of benzene, carbon tetrachloride, chloroform, toluene, methyl alcohol, and dichloroethane is studied experimentally. Investigations of the frequency dependence of the indicatrix form are carried out. Some theoretical aspects of the question are discussed and a comparison is made between the theory and experiment which reveals a satisfactory correspondence between the experimental data and the theoretical predictions.

The question of the angular dependence of Raman intensities was first investigated theoretically by Placzek, who obtained formulas for the indicatrix in the case of rotating molecules. Analogous formulas were derived later[2] by a simpler and more descriptive method. As for the experimental data, they are unfortunately incomplete at the present time. The first attempt at investigating the indicatrix form was undertaken by the authors.[3] These investigations were of a limited nature, but the principal fact is that the data obtained do not agree with the conclusions of the theory. In particular, in contradiction with the Placzek formula[1,2] it is found that $I(\varphi) \neq I(\pi-\varphi)$ ("forward-backward asymmetry"). Our investigations (also including the case of the 3062 cm^{-1} vibration of benzene, described in ref. 3), however, have not confirmed the presence of a substantial asymmetry (cf. [3]). The question of the intensity dependence on the scattering angle has also been experimentally studied in [4], where the data obtained confirmed the validity of the Placzek formula.

Information on the indicatrix form, emerging from the results of ref. 2, is still not complete. Consequently, we considered it expedient to undertake detailed investigations of it for a large number of different molecules and normal vibrations.

EXPERIMENTAL METHOD

The measurements were carried out with a method somewhat improved by comparison with ref. 2. The apparatus is schematically depicted in Fig. 1. Light from a PRK-4(S) exciting mercury lamp, supplied with ac by a VSO-50 ferroresonance stabilizer, fell on a cylindrical absorption cell K containing the liquid under investigation (M is a water jacket), after initially passing through a cylindrical diaphragm D (the maximum divergence of the beam after passing through the diaphragm did not exceed 1°). The scattered light entered a DFS-4 spectrograph through the slit S_p. The angular aperture of the objective-collimator was 8°20'. The widths of the entrance and exit slits were chosen to guarantee recording the integrated intensity of the scattered line. We also took account of the spectral sensitivity of the photomultiplier according to the method described in ref. 4. Hence the results of our measurements, presented below by means of graphs, are expressed in comparable units for each substance.

The source L, diaphragm D, and cell with the liquid were tightly connected to a common base and could be rotated about a vertical axis coinciding with the axis of the cylinder K, while the recording apparatus remained motionless. On a rotation of the operating apparatus the volume of the scattering liquid encompassed by the collimator aperture changed. This change was accounted for by a graphical method and corresponding corrections were introduced into the results obtained. The range of angles investigated was 40-150° in the majority of the cases, and the change of the observation angle φ in a rotation was 10°. All of the measurements were repeated at least ten times, whence the mean error was of the order of 5%.

In order to check the method, the indicatrix of the luminescence of a weak solution of fluoroscein (concentration 10^{-7} gm/cm^3) was measured. Because of Lommel's law, the indicatrix in this case must have a spherical form; this was obtained in the experiment (see Fig. 2).

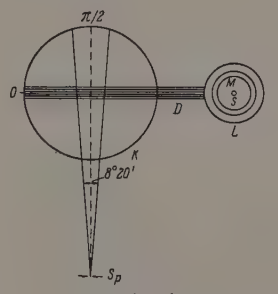

Fig. 1

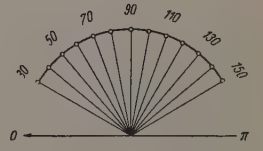

Fig. 2

Fig. 1. Schematic of the apparatus for the experimental study of the raman indicatrix.
Fig. 2. Luminescence indicatrix of a dilute water solution of fluoroscein ($\lambda_{exc.} = 4358$ A).

EXPERIMENTAL RESULTS AND THEIR COMPARISON WITH THE THEORY.

Broad experimental investigations of the indicatrix were carried out on the following sixteen vibrations of a series of different substances: 992, 1178, and 3062 cm^{-1} of benzene, 213, 313, 459 cm^{-1} of chloroform, 2832, 2944 cm^{-1} of methanol, 786, 1004 + 1030, 3051 + 3067 cm^{-1} of toluene* and 641, 689 cm^{-1} of dichloroethane. In addition in a whole series of cases the excitation was produced by

*In the last two cases we measured the summed integrated intensity of the two lines 1004 and 1030 cm^{-1}, and also of 3051 and 3067 cm^{-1}.

light of not one, but of several lines, as a result of which the dependence of the indicatrix form on the frequency of the exciting light was studied.

Before going into an analysis of the experimental results obtained we will dwell on some theoretical aspects of the question concerning the character of the Raman indicatrix. It has been shown[2] that in the case of natural incident light for freely rotating scattering centers the indicatrix form is defined by the following expression:

$$I(\varphi) \sim I_0 \frac{1}{15}(6A - B)\left(1 + \frac{2A + 3B}{6A - B}\sin^2\varphi\right) \qquad (1)$$

or, if we introduce the degree of depolarization ρ for observation at the angle $\pi/2$, it is equal to

$$\rho = \frac{2(A - B)}{4A + B}, \qquad (2)$$

$$I(\varphi) = I\left(\frac{\pi}{2}\right)\left(1 + \frac{1 - \rho}{1 + \rho}\cos^2\varphi\right). \qquad (3)$$

Here A and B are functions of the trace f and anisotropy g, invariants of the corresponding Raman tensor, where

$$A = \frac{1}{3}(f^2 + 2g^2), \qquad B = \frac{1}{3}(f^2 - g^2), \qquad (4)$$

and I_0 is the intensity of the incident light.

It follows from formulas (1)-(3) that the indicatrix form depends on the nature of the corresponding normal coordinate. The last dependence can be expressed in terms of the degree of depolarization ρ.

We will dwell further on one consequence of the theory. The components of the corresponding Raman tensor have the following form in the adiabatic approximation:

$$(\alpha_x)_{v, v\pm1} = -\frac{c^2}{\hbar\omega\omega_0}\sum_j{}' \left\{ \frac{2\omega'_{j0}}{\omega'^2_{j0} - \omega_0^2}\left[(S_x^{0j})_1 (S_x^{j0})_0 + (S_x^{0j})_0 (S_x^{j0})_1\right] \right.$$
$$\left. - 2\frac{\omega'^2_{j0} + \omega_0^2}{(\omega'^2_{j0} - \omega_0^2)^2}\left|(S_x^{0j})_0\right|^2 \left(\frac{\partial\omega'_{j0}(Q)}{\partial Q}\right)_{Q=Q_0}\right\}(Q - Q_0)_{v, v\pm1}. \qquad (5)$$

Here ω_0 and ω are the frequencies of the exciting and scattered radiation respectively, and the other symbols are the same as in ref. 5. The summation over j includes all excited electronic states, where to each j there belong two terms which correspond to dependences of the transition matrix element S^{0j} and of the frequency of the Franck-Condon transition ω'_{j0} on the normal coordinate.

In a series of cases several terms in expression (5) can simultaneously be substantial. Such a possibility exists if, for example, the number of essential absorption bands exceeds one. If far from the bands only one of them is at all essential, then on approaching a less essential band the latter's role can be significantly enhanced due to the presence of the resonance frequency denominators. Finally, it can happen that terms corresponding to the same j will be comparable in magnitude.

It is not hard to show that the quantities A and B can in the general case be written in the following manner:

$$A = \sum_i f_i(\omega_0) A'_i, \qquad B = \sum_i g_i(\omega_0) B'_i, \qquad (6)$$

where $f_i(\omega_0)$ and $g_i(\omega_0)$ are some functions of ω_0 which are expressed by the frequency factors, figuring in expression (5), by a definite model (depending on just which terms in (5) are substantial, i.e., it will be different for different specific cases). We note that the quantities A'_i and B'_i do not depend on ω_0. In those cases where one term dominates in relation (5), the sums figuring in formulas (6) also contain only one term.

The presence in expressions (6) of several terms can lead to the situation where the functions of the quantities A and B of type (2) are dependent on ω_0. This dependence will evidently be weaker than that of the fractions in the numerator and denominator of (2) separately. Obviously, it is weakened on recession of ω_0 from the absorption band, i.e., when the presence of ω_0 in the frequency factors of expression (5) becomes less substantial. If there is only one term in (6), the dependence of expressions of type (2) on ω_0 understandably vanishes.

From the preceding there emerges the possibility of a dependence of the indicatrix form and of the degree of depolarization on the frequency of the exciting light. It is also not hard to convince oneself that analogous conclusions will be valid even for the case of linearly polarized exciting light.

We will now progress to the analysis of the experimental data and their comparison with the theoretical predictions. First of all, one is struck (Fig. 3) with the dependence of the indicatrix form on the nature of the respective normal coordinate being in qualitative agreement with the theoretical conclusions. In addition, the indicatrix form is determined by the magnitude of the degree of depolarization ρ. Thus, for the 217 cm^{-1} line of CCl_4 and 1178 cm^{-1} line of C_6H_6, possessing a significant depolarization (from the data of refs. 6 and 7, ρ = 0.93 and 0.6 respectively), the indicatrix has a spherical and a nearly spherical symmetry. On the other hand, the stretching vibrations, 459 cm^{-1} of CCl_4 and 992 cm^{-1} of C_6H_6, for which the depolarization is close to zero,[7] give extended dumb-bell-like indicatrices. A fine illustration of the correspondence between the value of ρ and the indicatrix form is also provided by the chloroform case: the indicatrix for the 261 cm^{-1} line, for which ρ = 0.88,[7] is rather well given by a circle, while the indicatrices of the remaining two lines investigated ($\rho \approx 0.24$ and 0.05)[7] are extended in the direction of the exciting light beam. Analogous relationships, agreeing with the theory, are also observed in other cases.

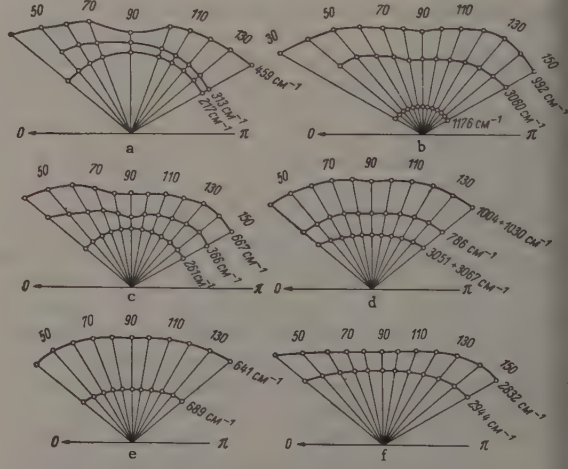

Fig. 3. Raman indicatrices for different normal vibrations of a series of molecules ($\lambda_{exc.}$ = 4358 A). Substance: a—CCl_4; b—C_6H_6; c—$CHCl_3$; d—$C_6H_5CH_3$; e—Cl_2HCCH_3; f—CH_3OH.

Experimental and Theoretical Values of the Function $I(\varphi)$

Substance	C_6H_6												$C_6H_5CH_3$					
$\lambda_{exc.}$ (A)	4358				4047				3650				3650		4047			
$\omega_{vib.}$ (cm^{-1})	992		3060		992		3060		992		1178		1004 + 1030		1004 + 1030		3051 + 3067	
φ (deg)	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
150	1.21	1.49	1.26	1.36	—	1.79	1.27	1.27	—	1.49	—	1.30	—	1.30	—	1.54	—	1.27
140	1.21	1.38	1.20	1.28	1.35	1.61	1.23	1.21	1.33	1.38	1.25	1.24	1.25	1.24	1.41	1.43	1.20	1.21
130	1.21	1.26	1.16	1.20	1.34	1.43	1.17	1.15	1.27	1.26	1.17	1.16	1.16	1.16	1.32	1.30	1.14	1.15
120	1.16	—	1.12	—	1.26	—	1.09	—	1.16	—	1.10	—	1.10	—	1.18	—	1.09	—
110	1.09	1.08	1.06	1.06	1.18	1.12	1.05	1.04	1.09	1.08	1.04	1.05	1.05	1.05	1.08	1.09	1.06	1.04
100	1.04	1.02	1.02	1.01	1.02	1.03	1.02	1.02	1.04	1.02	1.02	1.01	1.02	1.01	1.02	1.02	1.01	1.02
80	1.04	1.02	1.00	1.01	1.03	1.03	1.02	1.02	1.04	1.02	1.04	1.01	1.02	1.01	1.01	1.02	1.01	1.02
70	1.11	1.08	1.11	1.06	1.13	1.12	1.03	1.04	1.09	1.08	1.08	1.05	1.06	1.05	1.03	1.09	1.03	1.04
60	1.20	1.16	1.20	1.12	1.20	1.26	1.10	1.09	1.14	1.16	1.12	1.10	1.11	1.10	1.06	1.18	1.07	1.09
50	1.32	1.26	1.34	1.20	1.30	1.43	1.15	1.15	1.24	1.26	1.21	1.16	1.18	1.16	1.11	1.30	1.13	1.15
40	1.43	1.38	1.40	1.28	1.42	1.61	1.16	1.21	1.27	1.38	1.26	1.24	1.27	1.24	1.19	1.43	1.20	1.21

here was also discovered the presence of some ency dependence of the indicatrix form (a series of ples is presented in Fig. 4). As one would expect tter is not very significant, but all exceed the limits experimental error.* This question requires the-

as already been noted above, the magnitude of the ency dependence can serve as a qualitative indica- f how substantial is the influence of more than one simultaneously in formula (5). From the data given Table it emerges that the ω_0 dependence for the nd 3060 cm^{-1} vibrations of benzene is not very sub- al. This is an indirect confirmation of the correct- f the assumption (adopted in ref. 5) that in the cases oned the principal role is played by only one term pression (5).

cal and experimental investigations in the future.

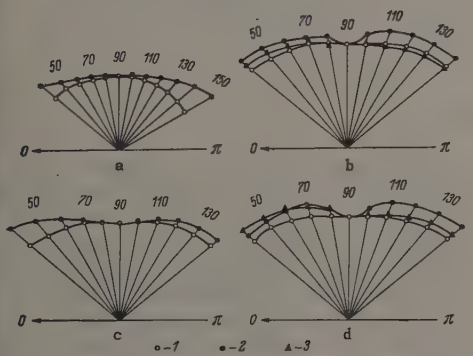

Fig. 4. Frequency dependence of the Raman indicatrix for a few normal vibrations of a series of substances. Substance and the frequency of the normal vibration (in cm^{-1}): a—C_6H_6, 1178; b—$C_6H_5CH_3$, 786; c—Cl_2HCCH_3, 689; d—Cl_2HCCH_3, 641. The wavelength of the exciting light (in A): 1—4358; 2—4047; 3—3650.

The agreement between theory and experiment with ect to the indicatrix form for a fixed exciting light ency is not only qualitative, but also quantitative. the corresponding choice of units the indicatrix is determined by the formula

$$I(\varphi) = 1 + C\cos^2\varphi, \qquad C = \frac{1-\rho}{1+\rho}. \qquad (7)$$

It is easy to see that the parameter C can be found is known. After this it is not hard to calculate the function $I(\varphi)$ using expression (7).* One can also deter-

*In ref. 2 values of $I(50°)$ which agreed well with the experimental values were calculated by this method for a few cases.

mine the magnitude of C from a known value of $I(\varphi)$ for a fixed φ. In view of a certain discrepancy and, in a series of cases, also from a lack of data on the depolarization, we have used the second possibility, determining the magnitude of C with the help of the experimental value of $I(120°)$. The magnitudes of $I(\varphi)$ calculated for the remaining values of φ are given in the Table, from which it follows that there is observed in general a satisfactory agreement between theory and experiment. At the same time the presence of some exceptions (while not very significant, but still exceeding the experimental error) is noted. In particular there is observed some forward-backward asymmetry in a series of cases, in which the intensity of the forward exceeds that of the backward scattered light. CCl_4 (459 cm^{-1} frequency), benzene (992 cm^{-1}), and chloroform (366 and 667 cm^{-1}) can serve as examples. In our opinion the indicated discrepancies arise first of all from the fact that the theory was developed for gases, while the experimental investigations were made in the liquid phase. The theory for the latter case is still not established.*

*The difference between conditions in the liquid and the gas case can be crudely accounted for if it is considered that the field E_D acting on the molecule differs from the average, $E_D = \chi E_{av}$, where the factor χ allows for this difference. The field acting on the molecule consists of an external and an induced field, arising from the presence of the surrounding molecules, in which the latter depends on their orientation, i.e., also on the orientation of the scattering molecule itself, since there is a correlation between it and its neighbors due to the maintenance of close order in the liquid. In other words χ depends on the position of axes rigidly fixed in the molecule relative to a motionless coordinate system. Therefore the result of averaging the expressions, determining the intensity of the scattered radiations, over all spatial orientations of the molecule will differ here from (1), since the expressions submitted to averaging will not be of the type (5) from ref. 2, as in the case of gases, but more complex functions containing χ. Further detailed investigations are still necessary along this direction, but this goes beyond the limits of the present work.

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INFRARED SPECTRA OF PHTHALOCYANINES
I. The Effect of Crystalline Structure and of the Central Metallic Atom on the Phthalocyanine Molecule in the Solid State

A. N. Sidorov and I. P. Kotlyar (pp. 175-184)

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The absorption spectra of sublimed layers of phthalocyanine without metal, ordinary and N-deuterated, and Met-phthalocyanines (Met = Mg^{II}, Zn^{II}, Cu^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Ag^{I}) in two different crystalline modifications have been investigated in the 400-3800 cm^{-1} region. An empirical interpretation of different absorption lines of the phthalocyanines is given. It is shown that the transition of the phthalocyanine without metal from α- to β-modification is associated with the lowering of the valence frequencies of the imino groups NH. It is concluded from this that the intermolecular hydrogen bonding in which these groups participate is strengthened with the transition $\alpha \rightarrow \beta$. The type of the central metallic atom in the Met-phthalocyanine molecule does not affect the properties of the crystalline lattice of the pigment but influences significantly the properties of the molecule.

Several absorption lines were found in this spectral region whose frequencies depend on the type of the central metallic atom, and this presents a possibility of the identification of phthalocyanines from their infrared spectra. The differences in the infrared spectra of the α- and β-modifications of the phthalocyanine also present a reliable method for identifying these modifications.

The infrared spectrum of phthalocyanine without metal (abbreviated H_2Phc, where Phc stands for the molecular skeleton of the pigment $C_{32}H_{16}N_8$) were obtained for the first time, in the form of suspension in Nujol, by Cannon and Sutherland.[1] Ebert and Gottlieb[2] investigated the infrared spectra of H_2Phc and MetPhc in Nujol (Met = Cu, Co, Ni, Zn). They found that the two different crystalline forms of the phthalocyanine were characterized by somewhat different spectra in the infrared region. From this they concluded that since the crystalline form of the pigment affects the infrared spectrum it also affects the intermolecular interactions in the substance. At the same time, depending on the crystalline form, the crystalline lattice energy as well as the energy of the individual bonds in the molecule may change. Kendall[3] confirmed the conclusion regarding the difference in the spectra of the α- and β-modifications of crystalline CuPhc. Later we studied in our laboratory the infrared spectra of the phthalocyanines with the aim of understanding their interactions with the vapors of different adducts.[4,5] It was shown that some MetPhc form molecular complexes with water, pyridine, hydrazine, and other compounds. It was assumed that the complex formation took place directly via the central metallic atom of the pigment molecule. In this and following articles the infrared spectra of the phthalocyanines are investigated with the purpose of obtaining additional data regarding the effect of the central metallic atom on the phthalocyanine molecule and the nature of complexes of the phthalocyanines with the adduct molecules.

EXPERIMENTAL PART

The phthalocyanines are not sufficiently soluble to obtain their infrared spectra in any solvent. Therefore, as in the past, the investigation of the spectra of the phthalocyanines had to be limited to the crystalline form. However, we rejected the method used previously by other authors which consisted of the preparation of the samples of the phthalocyanines by means of the dispersion in some immersion medium, since the latter not only results in the appearance of spectral lines which are characteristic to it but may also result in the additional complications related to the interaction of the phthalocyanine molecules with this medium. To prepare the phthalocyanine samples we made use of their property to sublime in vacuum at 400-500 C without detectable decomposition. The sublimation onto KCl or KBr plates from a specially grown crystal was carried out at 10^{-3}-10^{-4} mm Hg pressure in a glass cell previously described.[6] Before sublimation the plate was attached to a frame of iron wire, and in order to avoid warming up as well as to obtain a layer of homogeneous thickness it was suspended in the cell by means of a magnet 2-3 cm away from the crystal which was heated by a small oven. The temperature of the substrate during the sublimation of the pigment did not exceed 100° C. The duration of the sublimation was from three to six hours. After sublimation the cell was disconnected from the vacuum system the plate with the deposited layer of the pigment was placed into the space between the optical windows by

ple rotation of the tubular part of the cell, and the tra of the sample were then taken under vacuum litions. Using the same arrangement, it was also sible to obtain the infrared spectra of the layers of alocyanines in the presence of various gases and rs which had been purified from air and water vapor urities.

The spectra were taken in the region 400-3800 cm^{-1} e UR-10 spectrophotometer from the Zeiss Com- using KBr, NaCl, and LiF prisms.

The phthalocyanines were prepared in the Ivanov mical Technological Institute* using the method de-

are grateful to V. F Borodkin for supplying us with phthalocyanines.

ped by Linstead and co-workers.[7] We obtained chlo- ted CuPhc by passing gaseous chlorine for four hours - 50 mg of CuPhc in molten phthallic anhydride at C. The resulting mixture was vacuum distilled in a tz vessel. A pigment of bright green color (in trans- sion) began to sublime slowly at about 600° C and was sited on a KCl substrate for the study of its spectrum. chemical composition of the pigment thus obtained not controlled, but it is known[8] that under the given rimental conditions not less than fifteen atoms of rogen in the phthalocyanine molecule (from the total xteen) must have been replaced by chlorine atoms. We prepared the phthalocyanine without metal with erated imino groups by the exchange reaction of the nary H_2Phc powder with gaseous DBr in vacuum.

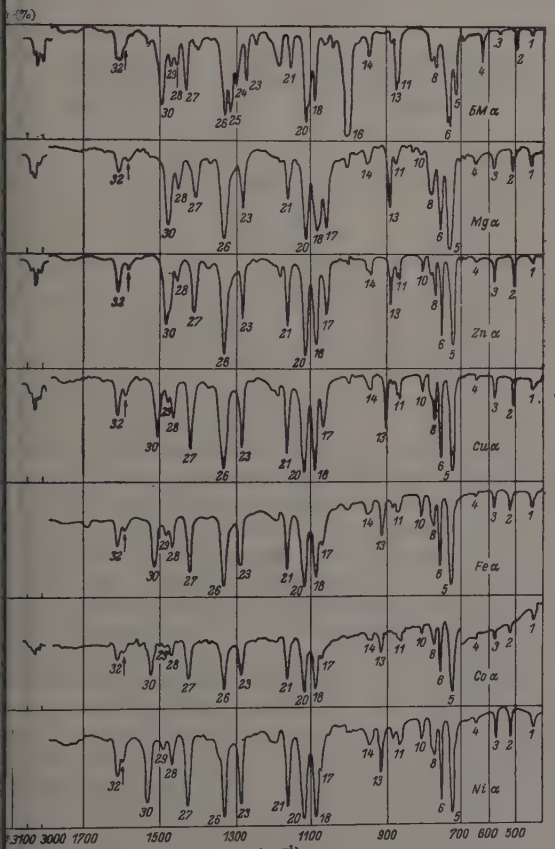

Fig. 1. The absorption spectra of the phthalocyanine layers condensed by sublimation (α-modification in vacuum).

The details of the method of deuteration will be described in the future communication. The phthalocyanine of silver does not sublime without decomposition when heated in vacuum. Therefore, for the spectral investigation each sample was prepared in a pellet form by pressing some of its fine powder with KBr.

THE EXPERIMENTAL RESULTS AND DISCUSSION

1. In Fig. 1 are shown the absorption spectra of the layers of H_2Phc and MetPhc (Met = Mg, Zn, Cu^{II}, Fe^{II}, Co^{II}, and Ni^{II}) taken in vacuum. The temperature of the KBr plates onto which the samples were sublimed did not exceed 100° C. The comparison of this spectra with the spectra of Zn-, Cu-, Co-, Ni-, and H_2Phc obtained by Ebert and Gottlieb[2] shows that the sublimation under the described conditions results in the crystalline α-modification of these pigments. The spectra of Mg- and FePhc were obtained by us for the first time. However, by analogy with other phthalocyanines it may be assumed that these phthalocyanines are obtained in the α-modification in this case. The spectral data (see below) support this assumption.

The heating of the phthalocyanine layers results in the gradual observable transition from α-modification into the more stable β-modification. Figure 2 shows the absorption spectra of the same layers as in Fig. 1 after they had been heated in vacuum. These spectra coincide

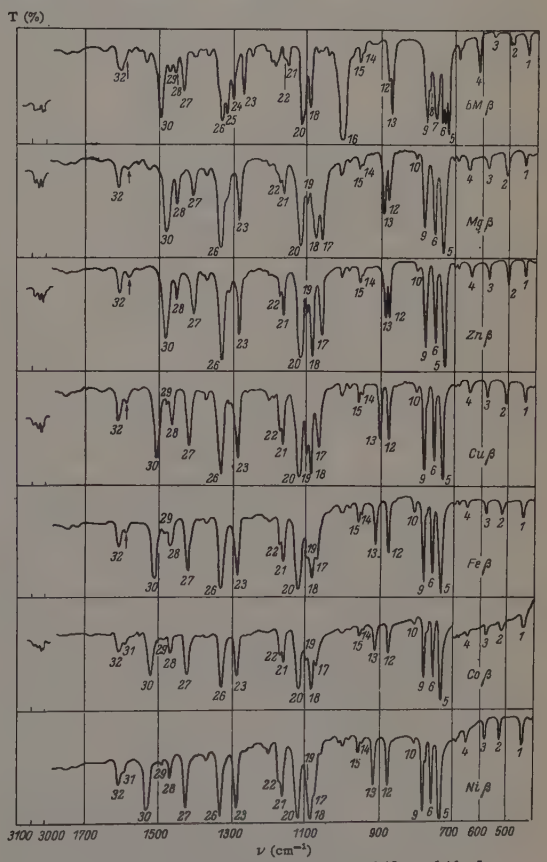

Fig. 2. The absorption spectra of the phthalocyanine layers condensed by sublimation (β-modification in vacuum). The same layers whose spectra are shown in Fig. 1.

with the spectra of phthalocyanines in the β-modification obtained by Ebert and Gottlieb. The rate of transition $\alpha \rightarrow \beta$ depends mainly on the temperature. In vacuum the rate of this transition is faster and takes place at lower temperature than in the atmosphere. There is a significant effect of the type of the central atom in the phthalocyanine molecule on the rate of this transition. For the complete $\alpha \rightarrow \beta$ transition in the case of Ni- and FePhc, the layers must be heated at 300° C for no less than five hours in vacuum. The complete $\alpha \rightarrow \beta$ transition in the case of H_2Phc was observed to take place after heating for six hours in vacuum at 280° C, and in the case of Mg-, Zn-, and CuPhc after two hours heating in vacuum at the same temperature. The heating of phthalocyanines in vacuum at temperatures exceeding 300° C is not possible because of their rapid sublimation. The layer of phthalocyanine may be found to consist of the mixture of both modifications if the heating of this layer is incomplete or does not take place at sufficiently high temperature. The completeness of $\alpha \rightarrow \beta$ transition could be controlled by noting the disappearance of the absorption lines characteristic for the α-modification (see below).

2. It is seen from the experimental data, shown in Table 1, and the comparison of Figs. 1 and 2 that the spectral characteristics of each phthalocyanine modification are practically independent of the type of the central atom. This is especially well illustrated in the case of β-modifications of the Met-phthalocyanines. The $\alpha \rightarrow \beta$ transition results in the appearance of new absorption lines in the spectra (shown in bold face print in Table 1) at 780, 877, 1100, and 1173 cm^{-1}, the position of which

Table 1. The Frequencies of the Absorption Lines of the Phthalocyanine Layers Condensed by Sublimation in Different Crystalline Modifications

Line No.	Phthalocyanines and their crystalline phase											
	Mg		Zn		Cu		Fe		Co		Ni		H_2	
	α	β	α	β	α	β	α	β	α	β	α	β	α	β
1	435	437	434	436	434	436	435	436	434	436	435	436	434	434
2	505		501		507		518		520		520		492	489 496
3	575		575		575		575		575		575		557	
4	642	644	640	638	643	641	644	645	645	645	646	645	620	616
5	728	731	721	728	722	730	726	734	726	734	726	734	714	720
6	752	754	752		754		756		756		756		730	736
7	—	—	—		—		—		—		—		—	783
8	*776*	—	*768*	—	*769*	—	*771*	—	*772*	—	*772*	773	*766*	771
9	—	**781**	—	**780**	—	**780**	—	**780**	—	**780**	—	**780**	778	**779**
10	801	801	800	800	802	802	804	803	805	805	806	804	—	—
11	*872*	—	*865*	—	*864*	—	*863*	—	*863*	—	*862*	—	*870*	—
			871	—	*870*	—	*868*	—	*868*	—	*867*	—		
12	—	**877**	—	**877**	—	**877**	—	**877**	—	**877**	—	**877**	—	**880**
13	890		888		900		910		915		917		874	873
14	949	949	*940*	—	*940*	—	*940*	—	*940*	—	*940*	—	946	952
			949	949	949	949	948	948	948	948	948	948		
15	—	**957**	—	**957**	—	**957**	—	**957**	—	**956**	—	**956**	—	**958**
16	—	—	—	—	—	—	—	—	—	—	—	—	1007	
17	1060	1059	1063	1062	1068	1067	1072	1073	1075	1076	1078	1078	—	
18	1086	1078	1091	1089	1092	1089	1089	1086	1092	1089	1091	1089	1094	1094
19	—	**1100**	—	**1103**	—	**1100**	—	**1098**	—	**1102**	—	**1100**	—	
20	1116	1118	1119	1120	1121	1123	1121	1123	1121	1123	1122	1123	1119	1119
21	1163	1162	1165	1164	1165	1164	1165	1164	1165	1165	1165	1165	1160	1156
22	—	**1173**	—	**1174**	—	**1174**	—	**1173**	—	**1174**	—	**1173**	—	**1163**
23	1283		1285		1287		1290		1291		1291		1277	
24	—		—		—		—		—		—		1311	
25	—		—		—		—		—		—		1321	1323
26	1333	1335	1334		1334		1333		1334		1335		1336	1334
27	1408	1407	1413	1410	1420	1419	1422	1422	1428	1427	1430	1428	1439	1437
28	1454	1451	1457	1455	1466	1465	1468	1468	1471	1471	1472	1471	1461	1459
29	—	—	—	—	1480		1484		1487		1493		1478	
30	1481	1478 1482	1480	1486	1507	1506	1516	1514	1526	1525	1536	1536	1503	1502
31	1586	1584	1586	1584	1591	1589	1592	1592	1597	1597	1600	1598	1600	1600
32	1609	1608	1611	1609	1611	1609	1611	1609	1612	1611	1612	1611	1610	1605
33	—		—		—		—		—		—		1617 3292	1613 3273

Note: The frequencies observed only in the spectra of the β-modification are in bold face print, while those observed in the spectra of the α-modification are italicized.

does not change significantly when one central atom is exchanged for another.

The characteristic spectral feature of the $\alpha \rightarrow \beta$ transition, besides the disappearance of the absorption lines characterizing the α-modification (the frequencies of these lines in Table 1 are shown in italics) and the appearance of the absorption lines characteristic of the β-modification, consists of the frequency shift of the absorption line No. 5 (see Figs. 1, 2, and Table 1) by several cm^{-1} in the direction of higher frequencies, followed by some intensification of this line. When the phthalocyanine layer consists of a mixture of the α- and β-modifications, then the absorption line No. 5 shows up as a doublet in the spectrum. The comparison of the relative intensities of the components of this doublet may be used as a sensitive spectro-analytical criterion for the estimation of the relative concentration of α- and β-modifications in mixtures. Besides the most evident spectral changes associated with the $\alpha \rightarrow \beta$ transition mentioned above, there are also some other changes (frequency shifts and change in intensity of absorption lines) which may be seen from the study of Figs. 1 and 2 and Table 1. In particular, changes are observed in the weak lines in the 3000-3100 cm^{-1} region corresponding to the vibrational valence frequencies of the CH bonds in the benzene rings of the phthalocyanines.

The coincidence of spectral characteristics of a given crystalline modification for all of the phthalocyanines shows that the type of the central metallic atom does not affect the properties of the crystalline lattice. It may be assumed that the inverse is also true: the crystalline form of the phthalocyanine does not affect the properties of the central metallic atom in the pigment molecule. The latter conclusion does not extend to H_2Phc in which the hydrogen atoms situated in the center of the molecule are affected by the interaction with the crystalline lattice of the layer. This interaction is evidenced by the frequency position of the absorption line corresponding to the vibrations of the imino groups NH—3292 cm^{-1} for α- and 3273 cm^{-1} for the β-modification. This particular spectral behavior of H_2Phc may be explained by the fact that the hydrogen atoms of the imino groups lie outside the plane of the phthalocyanine molecule, while the metallic atoms in the molecules MetPhc (Met-divalent metal) are situated in the same plane with the four surrounding atoms of nitrogen.[9]

It is not difficult to see that the spectrum of the β-modification of the phthalocyanines is somewhat more rich than the spectrum of α-modification in the number of the absorption lines and their intensity. It is possible that this is due to the more compact packing of the phthalocyanine molecules in the β-modification resulting in stronger intermolecular interactions than in the α-modification. As a consequence of the increased intermolecular interaction between the molecules of phthalocyanine associated with the $\alpha \rightarrow \beta$ transition some new absorption lines which were forbidden for the α-modification make their appearance in the β-modification. The intermolecular hydrogen bond in which the imino groups NH in the H_2Phc molecules evidently participate is strengthened with the $\alpha \rightarrow \beta$ transition, which is evidenced by the lowering in frequency of the valence vibrations of the groups NH with this transition.

3. The spectrum of phthalocyanine is significantly dependent on the symmetries of its molecules. To the molecule MetPhc (Met-divalent metal) in the free state, the point group symmetry D_{4h} (the symmetry of the

ire) may be assigned, if one assumes that the metallic h is bonded in the same way with all the four sur- nding nitrogen atoms. In the case of H_2Phc the molec- symmetry is lowered (at least down to the point up symmetry D_{2h}) due to the fact that the hydrogen ms of the imino groups are localized on the two hy- gen atoms in the trans-position with respect to each r.[10] In the solid phase the symmetry may be also red because of the intermolecular interactions which eir turn depend on the crystalline structure of the nent. The complexity of the phthalocyanine molecule, ther with the above-mentioned factors, leads to the llusion that a large number of frequencies in this ecule are lacking in characteristic constancy and r identification in the spectrum is very difficult.

The fundamental difference between the H_2Phc and Phc spectra cannot be exclusively explained by the rence in the symmetry of their molecules. It must upposed that the phthalocyanine molecule of the mono- nt silver possesses approximately the same sym- ry as the H_2Phc molecule. However, the spectra of e pigments (Figs. 1-3) differ very significantly from another. This shows that the central metallic atom ether with the symmetry properties of the molecule) a strong effect on the spectral characteristics of the nent and consequently also on the structure of its ecule. The effect of the central metallic atom on the alocyanine molecule consists in increasing the ac- y of this molecule with regard to the addition of the ct molecules.[4,5]

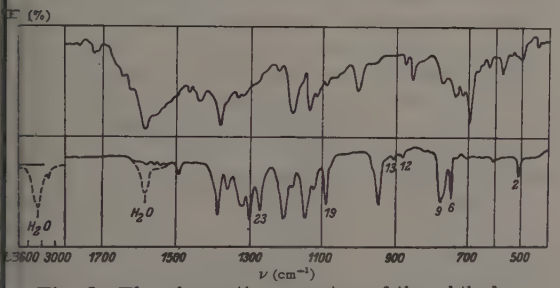

Fig. 3. The absorption spectra of the phthalocyanines. Top—silver phthalocyanine (KBr pellet in atmosphere); bottom—chlorinated CuPhc (in vacuum); broken curve—the same layer exposed to the atmosphere.

The spectra of MetPhc, with the exception of the sil- phthalocyanine, are very similar (Figs. 1, 2, and le 1). Among the spectra, however, there exist dif- nces which allow one to determine unambiguously type of the metal in the phthalocyanine. The absorp- lines corresponding to the vibrations of the N—Met to be found in the far region and are not accessible pectral investigation with the standard spectroscopic ipment. Nevertheless, in the investigated region of spectrum, there are several lines whose frequency ition significantly depends on the type of the central allic atom. They are the lines Nos. 13, 17, 23, 27-31 Table 1). All these lines are shifted to higher fre- ncies from one MetPhc to another in the order of the owing sequence: Mg-, Zn-, Cu-, Fe-, Co-, NiPhc. It y be assumed that the above-mentioned lines corre- nd to the vibrations of central atomic groups related he metallic atom either by direct bonding or indirectly ough a system of conjugated bonds. These lines, es- ially those which in the above-mentioned ordering se- quence of the phthalocyanines are shifted by a significant interval (lines Nos. 13, 27, and 30), may be used for spectroanalytical purposes in the identification of phthalocyanines in the solid phase. This identification may be made irrespective of the crystalline structure of a sample inasmuch as all the above-mentioned lines differ but little in frequencies in the transition from one crystalline modification to another.

4. Let us try to give an interpretation to the individual absorption lines in the infrared spectra of the phthalocyanines based on the comparison of their vibrational frequencies with the characteristic vibrations of different bonds in other molecules.[11]

The intense line No. 5 situated at about 714 cm^{-1} in the spectrum of the α-modification of H_2Phc and in the region 721-728 cm^{-1} (Table 1) in the spectra of the α-modification of MetPhc corresponds to the out-of-plane deformational frequencies of the CH bonds in the benzene rings. The same interpretation of this line was made by Kendall[3] in the case of CuPhc. The absence of the line No. 5 in the spectrum of chlorinated CuPhc confirms such an interpretation of this line. The line No. 5 in the spectra of all phthalocyanines with the $\alpha \rightarrow \beta$ transition is shifted by several cm^{-1} towards higher frequencies. In the spectrum of H_2Phc in the neighborhood of the line about 714 cm^{-1} there is a doublet line No. 6. Inasmuch as the latter does not change with the $\alpha \rightarrow \beta$ transition, it is the line at 714 cm^{-1} and not the line No. 6 which must be attributed to the vibrations of the CH bonds in the H_2Phc molecule.

The line No. 6 found in the spectra of MetPhc in the vicinity of 755 cm^{-1} is conserved in the spectrum of CuPhc after the chlorination (Fig. 3), from which it follows that this line is not related to the vibrations of the CH groups. A very intense absorption line at about 1007 cm^{-1} (No. 16) is observed in the spectrum of H_2Phc. In the same region there is a line of medium intensity at 1005 cm^{-1} in the spectrum of silver phthalocyanine. In the spectra of MetPhc the corresponding line is absent (probably because it is being forbidden by the higher symmetry of these molecules). The absorption line in the vicinity of 1610 cm^{-1} (No. 32) probably corresponds to the valence vibrations of the C—C conjugated bonds of the benzene rings.

The spectrum of the chlorinated CuPhc (Fig. 3) was obtained by us with the aim of identification of the absorption lines corresponding to the vibrations of the CH bonds in the benzene rings of the phthalocyanines. However, as may be seen from the comparison of the spectra, the chlorination of phthalocyanine leads to such significant spectral changes that most of these changes are hard to interpret without additional investigation. Let us note in passing that the chlorinated CuPhc, in contrast to the ordinary one, is capable of adding to itself water molecules from the atmosphere. To the molecules of water thus bonded to the chlorinated CuPhc correspond the absorption lines with the maxima at 1588 cm^{-1} (deformational vibration) and at 3380 cm^{-1} (valence vibration). These lines disappear when the sample is dried in vacuum and reappear again when it is exposed to the atmosphere.

With the aim of identification of the absorption lines related to the vibrations of the imino groups NH we obtained the spectrum of the N-deuterated phthalocyanine without metal. A comparison of this spectrum with that of H_2Phc (Fig. 4) shows that the deuteration of phthalocyanine without metal leads to the appearance of a greater number of lines in comparison with the number of lines

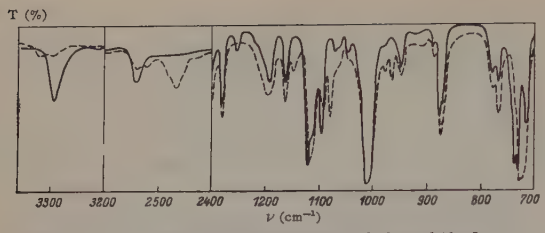

Fig. 4. The absorption spectra of the phthalocyanines without metal. Solid curve—ordinary phthalocyanine; broken curve—N-deuterated phthalocyanine.

which have disappeared. This is probably due to the fact that our sample contained an admixture of half-deuterated HDPhc molecules in addition to the completely deuterated molecules D_2Phc. The comparison of intensities of the absorption lines corresponding to the valence vibrations of the imino group (Table 2 and Fig. 4) shows that the sample investigated by us contained at least 70% D_2Phc. The remaining 30% were HDPhc and H_2Phc.

Regarding Table 2 and Fig. 4 we must make the following remarks.

In the spectrum of deuterated phthalocyanines there is an intense line at 1076 cm^{-1} but its analog was not found in the H_2Phc spectrum. Significant changes take place in the 700-740 cm^{-1} region following the deuteration of H_2Phc. Because of the superposition of lines and the dependence of the above-mentioned changes on the crystalline modification of the pigment their interpretation is difficult. The intense line at 753 cm^{-1} in H_2Phc, observable only in the spectrum of the β-modification, disappears after deuteration. Instead of it there remains a comparatively weak line at 758 cm^{-1} which may be attributed to the admixture of HDPhc in the sample. The analog of the 753 cm^{-1} line in the spectrum of D_2Phc is probably the line at 550 cm^{-1}, although its intensity is markedly lower than that of the 753 cm^{-1} line. It is possible that these lines are related to the deformational frequencies of the imino groups which are allowed only in the case of the β-modification of phthalocyanines without the metal.

Table 2. The Frequencies of the Absorption Lines of the Phthalocyanines without Metal Related to the Vibrations of Imino Groups (in cm^{-1})

Lines of groups NH		Lines of groups ND		Interpretation and remarks
α-modification	β-modification	α-modification	β-modification	
3292	3273	2466	2456	Valence vibrations of imino groups H_2- and D_2PhC
3317	3297	~2480	2467	Valence vibrations of imino groups HDPhC
1539		1144		Deformational frequencies of imino groups
		962		
1250		976		
—		1076		
—	753	—	550	The line characterizes only the β-modification
736		~720		
—	—	540	—	Very weak lines
—	—	522		
—	—	482		

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FREQUENCIES AND INTENSITIES OF THE ABSORPTION BANDS OF MONOSUBSTITUTED BENZENES IN THE REGION OF THE STRETCHING VIBRATIONS OF C—$H_{arom.}$ BONDS

M. P. Lisitsa and I. N. Khalimonova (pp. 185-191)

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The absorption spectra of five monosubstituted benzenes (toluene, nitrobenzene, aniline, chlorobenzene, and bromobenzene) have been studied in the region of the stretching vibrations of C—H bonds. An interpretation of the observed bands is given and the frequencies of their maxima, their integrated intensities, and their half-widths are determined. The vibrations entering into Fermi resonance are established. It is found that, as the electronegativity of the substituent increases, the intensity of the stretching vibration of the C—$H_{arom.}$ bond falls while the frequency rises. The indicated dependences are approximately linear in character.

RODUCTION

In recent years, one of the most pressing problems vibrational spectroscopy has been the problem of the nperature dependences of the infrared absorption spec- and Raman spectra of molecular compounds. Clari- ation of the role of the specificity and form of intra- lecular vibrations is very important for its solution. s therefore of interest to engage in a study of those ds whose vibrations are distinguished by a relatively h specificity and a clearly marked form. The stretch- vibrations of the C—H bonds of aromatic hydrocar- s are definitely of this sort. Numerous experiments e shown that, in the region of the vibrations men- ned, the absorption spectra are distinguished by a rich ucture brought about by the appearance of overtones l combination frequencies. As a result of resonance eraction, the intensities of some of them may come se to the intensities of the bands of the fundamental rations. The latter circumstance, and also the over- ping of the bands, often make difficult the interpreta- n of the separate maxima and the establishment of the ues of the true frequency, integrated absorption, and lf-width. Nevertheless, such data are necessary even ore setting up temperature experiments, since their ence may considerably complicate, or even make im- sible, the interpretation of the temperature depen- nces.

The present work pursues the goal first of all of ving the particular problem indicated above. However, choice of objects of study enables us to make a par- el study of the question of the interrelation of the in- sities and frequencies of the C—H stretching vibra- ns with the polarity of the molecules and the electro- gativity of the atom or group of atoms which replace a drogen atom on the benzene ring. It is evident that, on ch substitutions, the entire spectrum undergoes cer- n changes, but in what follows we shall keep in view ly the region of the C—$H_{arom.}$ stretching vibrations.

So far as is known to the authors, this question has en almost unstudied, although its solution can give in- rmation useful not only for spectroscopy, but also for ructural and theoretical chemistry. As Bykov has own[1] on the basis of his own and literature data, the ectronegativity values of the atoms exert a direct in- ence on the mechanical and electro-optical parameters the chemical bond. In certain groups of compounds, example, a linear relation between the frequency of the C—H stretching vibrations and the electronic charge of the bond has been established. This relation may be used to estimate the degree of specificity of a vibration, to obtain an analytical connection between the electronic charges of chemical bonds and their force constants, etc.

There is in the literature a considerable amount of information on the infrared absorption of monosubstituted benzenes in the spectral region of interest to us. However, this information is not of a quantitative character and has almost always been obtained for solutions. Therefore, we shall refer below to the separate works only in case their results may be introduced for comparison or used in the interpretation of data obtained in the present work.

RESULTS OF THE MEASUREMENTS

The measurements were made on an IKS-6 spectrophotometer. The spectral slit width (LiF prism) did not exceed 6 cm^{-1}. To exclude the influence of repeated reflections, the portion of the spectrum under study was measured with two cells whose thicknesses differed by roughly a factor of two. The determination of the thickness was carried out by the interference method with an error of 2-3%. In each case, the final absorption curve was obtained as the result of averaging five recordings. The error in the determination of the absorption coefficient did not exceed 3-5%. The integrated intensity and the halfwidth were measured, in the majority of cases, with an accuracy of 7-10%. To avoid the perturbing influence of impurity molecules on the vibration under study and the appearance of "false" maxima, all the substances were subjected to a preliminary careful purification, being distilled once more in vacuo just before the measurements.

The results obtained are shown in Fig. 1 in the form of absorption curves. The identification and symmetry of the vibrations corresponding to the observed bands are presented in Table 1. The values of the half-width Γ, the absorption coefficient at the maximum K_{max}, and the integrated absorption S of the bands are also shown there. In those cases when an unequivocal separation of strongly overlapping bands is difficult, tentative data on the quantities S and Γ are presented.

Because of the presence of the methyl group, the greatest number of bands was recorded for toluene ($C_6H_5CH_3$): the bands of no less than 7 vibrations fall into

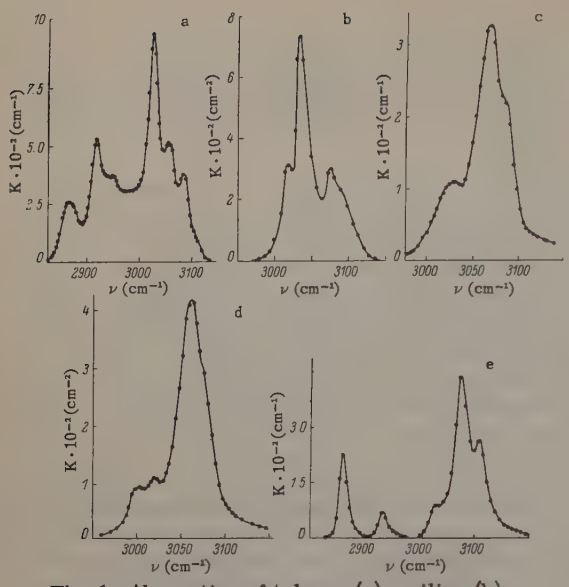

Fig. 1. Absorption of toluene (a), aniline (b), bromobenzene (c), chlorobenzene (d), and nitrobenzene (e) in the region of the C—$H_{arom.}$ stretching vibration.

the investigated region of the spectrum (Fig. 1a), two of them being distinguished by their pronounced intensities—$\nu = 2919$ and 3026 cm^{-1}. The weakest band, $\nu = 3110$ cm^{-1}, is observed clearly only on lowering the temperature to the freezing point. The spectrum of aniline ($C_6H_5NH_2$) is simpler (Fig. 1b): at room temperature one can find four bands, of which only three are characterized by clearly marked maxima.

In spite of the analogous structure of the molecules, the spectra of chlorobenzene (Fig. 1c) and bromobenzene (Fig. 1d) are not entirely similar to each other. If only one maximum is observed for the first of these substances in the longer-wavelength (relative to the fundamental ban region, two maxima, approximately equal in intensity, appear clearly for the second. It is not difficult to note that the fundamental band of chlorobenzene overlaps another weaker band on the short-wavelength side. For bromobenzene, one can only guess at a similar overlapping on the basis of the asymmetry of the absorption ban In the solid phase, the two spectra are entirely identical and remind one of the spectrum of liquid chlorobenzene, but with sharper maxima.

The spectrum of nitrobenzene ($C_6H_5NO_2$) (Fig. 1e) is similar to the chlorobenzene spectrum, although in th former it is not the long-wavelength satellite but the short-wavelength one which manifests itself more distinctly. In a somewhat longer-wavelength region of the spectrum (relative to the one studied), we have found two fairly intense absorption bands which are characterized by a significant temperature dependence. These bands have no relation to the vibrations studied in the present work, but the circumstance noted above and their direct proximity to the studied portion of the spectrum to a cer tain extent justify their examination.

DISCUSSION OF RESULTS

For an assignment of the observed bands, it is necessary to know the symmetry groups of the molecules of the substances studied. As is well known, the chloro- and bromobenzene molecules belong to the point group C_{2v}. The nitrobenzene molecule is apparently also to be assigned to the same group, since the most probable configuration of the NO_2 group corresponds to the placement of the oxygen atoms in the plane of the benzene rin Energetically, such a placement is more stable than others, since it guarantees a stronger interaction between the oxygen atoms and the nearest hydrogen atoms. The hydrogen atoms in the NH_2 group of the aniline molecule must be differently located. In view of the presence of repulsive forces, the plane of the HNH triangle

Table 1. Frequency Assignment of the Vibrations of Monosubstituted Benzenes and Fundamental Characteristics of the Corresponding Absorption Bands at Room Temperature (Spectral Region $\nu = 2800$-3200 cm^{-1})

Substance	Vibration	$2\delta_{as}CH_3$	$\nu_s CH_3$	$\nu_{a'} CH_3$	$\nu_{a''} CH_3$	$\nu CH_{arom.}$	$(\nu_s + \nu_a)_{NO_2}$	$(\nu_2 + \nu_4)_{CC}$	$2\nu_2 CC$	$(\nu_3 + \nu_4)_{CC}$	$(\nu_1 + \nu_4)_{CC}$	$(\nu_1 + \nu_2)_{CC}$	$(\nu_1 + \nu_3)_{CC}$
		Symmetry											
		A	A	E	—	A_1	B_1	B_2	A_2	A_2	B_1	B_1	A_1
$C_6H_5CH_3$	$\nu_{obs.}$ (cm⁻¹)	2868	2919	2952	2980 *	3026	—	—	—	—	3060	3080	3110
	$\nu_{calc.}$ »	2900	—	—	—	—	—	—	—	—	3057	3084	3100
	K_{max} ** »	270	510	320	~200	980	—	—	—	—	450	320	~ 60
	Γ »	34	26	—	—	29.5	—	—	—	—	25	25.5	—
	S (cm⁻²)	10000	16500	—	—	30300	—	—	—	—	11900	8800	—
$C_6H_5NH_2$	$\nu_{obs.}$ (cm⁻¹)	—	—	—	—	3036	—	—	3013	—	3072	3087	3108 *
	$\nu_{calc.}$ »	—	—	—	—	—	—	—	3000	—	3070	3089	3102
	K_{max} »	—	—	—	—	720	—	—	60	—	~180	~160	—
	Γ »	—	—	—	—	20	—	—	10	—	—	—	—
	S (cm⁻²)	—	—	—	—	21100	—	—	1600	—	2880	~3900	—
C_6H_5Br	$\nu_{obs.}$ (cm⁻¹)	—	—	—	—	3060	—	—	—	3000	3020	—	3077 *
	$\nu_{calc.}$ »	—	—	—	—	—	—	—	—	3006	3026	—	3058
	K_{max} »	—	—	—	—	410	—	—	—	65	55	—	—
	Γ »	—	—	—	—	33	—	—	—	24	14	—	~ 23
	S (cm⁻²)	—	—	—	—	17500	—	—	—	1920	720	—	~3000
C_6H_5Cl	$\nu_{obs.}$ (cm⁻¹)	—	—	—	—	3065	—	—	—	3000 *	3020	—	3077
	$\nu_{calc.}$ »	—	—	—	—	—	—	—	—	3018	3032	—	3064
	K_{max} »	—	—	—	—	320	—	—	—	—	~60	—	
	Γ »	—	—	—	—	32	—	—	—	—	~22	—	
	S (cm⁻²)	—	—	—	—	15200	—	—	—	—	1660	—	~1800
$C_6H_5NO_2$	$\nu_{obs.}$ (cm⁻¹)	—	—	—	—	3072	2859	2932	—	3029	—	—	3110
	$\nu_{calc.}$ »	—	—	—	—		2864	2937	—	3048	—	—	3088
	K_{max} »	—	—	—	—	405	230	67	—	60	—	—	200
	Γ »	—	—	—	—	30	20	22	—	26	—	—	32
	S (cm⁻²)	—	—	—	—	12600	4300	1450	—	1630	—	—	7200

* Observed at lower temperatures.
** The values of K_{max}, Γ, and S were determined for the separated bands.

erpendicular to the plane of the benzene ring. As a lt, we obtain a structure whose symmetry is the e as in the preceding cases.

If the rotation of the methyl group is not free, the ne molecule may be represented by the point group In this case, one of the edges of the base of the midal CH_3 group (the pyramid will not necessarily egular) is parallel to the plane of the benzene ring. e rotation relative to the C—C bond is completely , then the whole CH_3 group may be considered as a rate atom, and the toluene molecule may be assigned e symmetry C_{2v}. Then the vibrations associated with benzene ring and the methyl group are best studied rately: the first on the basis of the group C_{2v}, the nd on the basis of the group C_{3v}. Under this condi- one stretching vibration of the CH_3 group will be ly symmetric and the second doubly degenerate. attachment of the group under consideration to the ene ring is apparently accompanied by its partial rmation, and at the same time by the removal of the eneracy (this is all the more plausible for the con- ed state). Experiment confirms this supposition: in region of the C—H stretching vibrations, three ab- tion bands are observed in place of two.

In assigning the frequencies, we have been guided he considerations presented above. Since the bands ne first overtones and combination frequencies of the C bond stretching vibrations fall into the investigated ion of the spectrum (the fundamental frequencies of e are located in the region $\nu = 1400\text{-}1600\ cm^{-1}$, h we did not study), the averaged data of refs. 2 and the frequency values of the vibrations mentioned e used for the identification of the respective maxima le 2).

Table 2. Literature Data (Frequencies in cm^{-1}) on the Absorption of Monosubstituted Benzenes in the Region $\nu = 1400\text{-}1600\ cm^{-1}$

Compound	Reference	ν_1CC A_1	ν_2CC B_1	ν_3CC A_1	ν_4CC B_1
Toluene	[2]	1603	—	1496	1455
	[3]	1605	1588	1496	1460
Aniline	[2]	1605	1563	1495	1465
	[3]	1603	1591	1500	1467
Bromobenzene	[2]	1581	1563	1477	1446
	[3]	1580	1570	1475	1443
Chlorobenzene	[2]	1587	1562	1479	1447
	[3]	1585	1570	1478	1446
Nitrobenzene	[2]	1609	1590	1478	1458
	[3]	1608	1591	1480	1457

For all five materials, the value of the type A_1 (A′) ation frequency of the C—$H_{arom.}$ bond is included in relatively broad limits, namely, $\nu = 3026\text{-}3076\ cm^{-1}$, increasing from toluene to nitrobenzene (Table 1). s the vibration under consideration is not strictly racteristic with respect to frequency, since the influ- e of the substituent group on it is quite apparent. e intensity changes in the opposite direction; i.e., it inishes in the same sequence of substances. This de- ase is fairly marked (a factor of ~2.5), so that the cificity of this vibration with respect to intensity can o not be denoted as high. We shall dwell in more de- on these questions after an analysis of certain pecu- rities of the spectra obtained.

The absorption of toluene (Fig. 1a) in the spectral ion $\nu = 2800\text{-}3000\ cm^{-1}$ is brought about by vibrations the CH_3 group (frequencies, interpretation, and symmetry are presented in Table 1). The relatively high intensity of the band of the first overtone of the antisymmetric vibration δ_{as} attracts attention. The integrated absorption in the $2\delta_{as}$ band is less by a factor of only 1.7 than the same quantity for the fundamental vibration ν_s ($\nu = 2919\ cm^{-1}$). Furthermore, the difference between the calculated and observed frequency values of the overtone ($\Delta\nu = 32\ cm^{-1}$) cannot be explained by the effect of mechanical anharmonicity, since it is too large. Both these facts testify to the presence of Fermi resonance, the conditions for which are sufficiently favorable in this case, between the vibrations $2\delta_{as}$ and ν_s.

It is difficult to explain by resonance interaction the significant intensities of the bands corresponding to the combination frequencies $\nu_1 + \nu_4$ and $\nu_2 + \nu_3$ of the C—C bond, on account of the nonfulfillment of the condition that the wave functions have the same symmetry. At the same time, it is no less difficult to visualize such an absorption without a substantial influence of certain factors on the indicated vibrations. The question of their intensities remains open for the present.

The excess (by about 20 cm^{-1}) of the observed frequency value over the calculated one for the $\nu_1 + \nu_3$ vibration of the C—C bond in the case of chlorobenzene, bromobenzene, and nitrobenzene, and by 6 cm^{-1} in the case of aniline, may be brought about only by resonance, since in the absence of resonance the observed frequency value would have to be less than the calculated one as a result of mechanical anharmonicity. The presence of resonance is also confirmed by the quite intense absorption in the bands of the combination frequency $\nu_1 + \nu_3$. We note also that a shift of the absorption maxima on account of resonance always leads to an increase in the distance (as compared with the calculated distance) between the bands of the fundamental and combination frequencies, which is also observed in our case.

For the assignment of the two longest-wavelength absorption bands of nitrobenzene, we shall make use (in addition to the data presented in Table 2) of the results of ref. 4 concerning the values of the symmetric and antisymmetric stretching vibration frequencies* of the NO_2 group, which equal 1347 and 1527 cm^{-1} respectively. The more intense band $\nu = 2859\ cm^{-1}$ is the additive combination of these fundamental vibrations, and the less intense one may be ascribed to the combination $\nu_3 + \nu_4$ (C—C).

*The frequency values presented in ref. 4 refer to a CCl_4 solution. Since this solvent is not polar, the change in the vibration frequencies will apparently be small. Direct comparison of the spectra obtained in the present work with the solution spectra also speaks in favor of this conclusion.

Let us return finally to the question of the interrelation of the electronegativity of the substituent with the position and intensity of the bands belonging to the C—$H_{arom.}$ bond vibrations, and to the elucidation of the influence of the molecular dipole moment on these characteristics. As follows from Table 3, a change in the dipole moment has the same qualitative influence on the frequency and intensity values as a change in the electronegativity of the substituent. Only the case of the transition from bromobenzene to chlorobenzene is an exception, being accompanied not by an increase in the dipole moment (in accordance with the increase in electronegativity) but by its decrease.

It follows from Fig. 2 that the intensity and frequency values for the bands of the C—$H_{arom.}$ bond stretch-

Table 3. Comparison of the Frequency, Intensity, and Half-Width Values of the Band of the C—$H_{arom.}$ Stretching Vibration of Monosubstituted Benzenes with the Molecular Dipole Moments and Electronegativity Values of the Substituents

Substance	$C_6H_5CH_3$	$C_6H_5NH_2$	C_6H_5Br	C_6H_5Cl	$C_6H_5NO_2$
$\nu C-H_{arom.}$ ($см^{-1}$)	3026	3036	3060	3065	3076
$S \cdot 10^{-3}$ ($см^{-2}$)	30.3	21.1	17.5	15.2	12.6
$\frac{\Gamma}{S} \cdot 10^3$ (см)	0.98	0.9	1.9	2.1	2.2
μ* (D)	0.39	1.51	1.73	1.56	3.99
E**	—3.8	—1.2	2.8	3.0	4.0

*Dipole moment values are taken from ref. 5.
**Electronegativity values calculated according to Pauling's data.[6]

ing vibrations depend linearly on the electronegativity of the substituent groups: with an increase in the latter, the intensity diminishes while the frequency increases. Such relationships may apparently be interpreted in the following way. The electron-donating groups CH_3 and NH_2, by giving up a part of their charges to the benzene ring, favor an increase in the electron density in the latter. Therefore, the C—H bonds acquire a more ionic character, and the intensity of the bands of the vibrations under consideration increases. On the other hand, the flow of π-electrons out of the ring toward the electrophilic substituents (NO_2, Cl, Br) leads, in particular, to a lowering of the charge and dipole moment of the C—H bonds, which brings about a reduction of the intensity of the bands of the corresponding vibrations.

The value of the characteristic vibration frequency of an individual bond may be considered, to a crude approximation, as proportional to the square root of a force constant. For the substances considered here, the length of the C—$H_{arom.}$ bond remains constant, so that the stiffness constant of the bond must be determined to a considerable degree by its charge. Consequently, the directly opposite effect is to be expected—not an increase, but a decrease in the vibration frequency. This contradiction

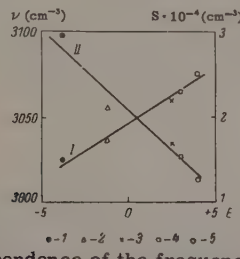

Fig. 2. Dependence of the frequency at the maximum (I) and the integrated absorption (II) in the band of the C—$H_{arom.}$ vibration on the electronegativity of the substituent. 1—$C_6H_5CH_3$; 2—$C_6H_5NH_2$; 3—C_6H_5Br; 4—C_6H_5Cl; 5—$C_6H_5NO_2$.

is brought about not only by the absence of high specificit and the impossibility of considering an individual C—H bond as a diatomic molecule, but also by intermolecular interactions, which limit to a considerable degree the justice of such considerations.

With an increase in the electronegativity of the groups replacing a hydrogen atom on the benzene ring, the intermolecular interactions also increase. It is therefore to be expected that the value of the ratio Γ/S will increase in the order toluene-nitrobenzene; i.e., the band will become relatively more diffuse. Analysis of the third line of Table 3 in general confirms this position.

CONCLUSIONS

1. For the monosubstituted benzenes investigated, shifts in the maxima of the absorption bands of certain overtones and combination frequencies, and also their intensity values, are explained by resonance interaction of the corresponding vibrations.

2. An increase in the electronegativity of the atom (or group of atoms) replacing a hydrogen atom on the benzene ring is accompanied by an increase in the frequency of the C—$H_{arom.}$ stretching vibration and a decrease in the intensity of the corresponding band. Both dependences are practically linear in character. The second of them is explained by a parallel decrease in the dipole moment of the C—$H_{arom.}$ bond.

3. The diffuseness of the band contour of the C—$H_{arom.}$ valence vibration depends directly on the electronegativity of the substituent, since an increase in the latter is accompanied by an intensification of intermolecular interactions.

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SHAPE OF THE VIBRATIONAL ABSORPTION BAND CONTOURS OF LIQUID CHLOROFORM AND BROMOFORM

Yu. P. Tsyashchenko (pp. 192-195)

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The vibrational absorption band contours have been investigated for liquid chloroform (vibrations ν_4 and ν_5) and bromoform (ν_2, ν_4, and ν_5). It has been shown that the shape of the bands corresponding to the ν_2 and ν_4 vibrations of the molecules under investigation is described with a high degree of accuracy by the dispersion formula. The bands of the ν_5 vibration are characterized by a contour very close to a Gaussian one.

The question of the shape of vibrational band con- is one of the most important in theoretical molec- spectroscopy. Without a knowledge of the function n describes the contour, it is not possible to allow[1-7] e apparatus distortions introduced into the observed parameters in consequence of the finite resolving r of the spectrophotometers. On the other hand, the contour is very sensitive to various kinds of external nces,[9-11] for which reason the study of its varia- may prove to be the source of important informa- when intermolecular interactions are being considered. while, the above-mentioned question has been almost letely uninvestigated.

The data contained in certain early works (see, for ple, ref. 12) are as a rule of low reliability, since were obtained using instruments with a large spec- slit width, and the procedure for taking account of ffect of the latter had not yet been sufficiently de- ed at that time. Trustworthy results have been pub- d only in recent years and in small quantity.[1,2,4,7,8] ould moreover be emphasized that, in the majority ses,[2,4,7] the shape of the bands was established by direct method, principally by the agreement of the ved contours with the calculated ones, after previous ction for the spectral slit width. Here the calcula- were based on a priori assumptions concerning the e of the contour. The direct determination of the using grating spectrophotometers of high resolu- as been carried out only in ref. 8 and, in part, in 1.

In connection with the foregoing, the quantitative data ned by us for the bands of the ν_2, ν_4, and ν_5 funda- al vibrations of liquid $CHCl_3$ and $CHBr_3$ are of defi- interest.

The measurements were carried out using an IKS-6 trophotometer. The geometric slit width was meas- with a microscope, while the spectral width was uted according to the familiar two-term formula.[2,7,13] formula was derived for an ideal apparatus. Never- ss, a special check has shown[14] that it can be suffi- ly well applied to spectrophotometers of types IKS-11 KS-6. The latter in particular is confirmed by our urements also: the observed splitting (2.5 cm^{-1}) of ong-wavelength component of the ν_4 vibration in talline $CHCl_3$,[11] the magnitude of which is just at the of real resolution of the IKS-6 instrument, agrees factorily with the computed value of the spectral slit n, which equals 2.8 cm^{-1}.

The procedure employed in the present work for titative absorption measurements has previously described in detail.[15] We shall only mention that, in order to eliminate selective reflection, we made use of pairs of cells of different thicknesses, the values of which were determined, within the 5-400 μ interval, by an interference method with an error of ~1%. The "effective" thickness below 5 μ was measured according to the method described in ref. 16.

In the study of the contour, it is particularly important to obtain the exact distribution of the absorption in the wings of the band where, as is well known, the differences among the possible shapes of the contours are greatest. Therefore, each band was studied using a set of cells whose thicknesses were chosen in such a way, depending on the optical density, as to satisfy the conditions of minimum relative error and maximum contrast of the record[17] in a given part of the contour. The total error in the computation of the absorption coefficients did not exceed 5-10%. The regions of greatest absorption near the maxima of the ν_5 vibration bands, where it may reach 15-20%,[16] constitute an exception.

The experimental results are represented in Figs. 1 and 2 by points of different shape (for different cell pairs). Since the inequality $\Delta\nu_s/\Gamma < 0.2$-0.25 was fulfilled for all the bands studied (Γ is the observed half-

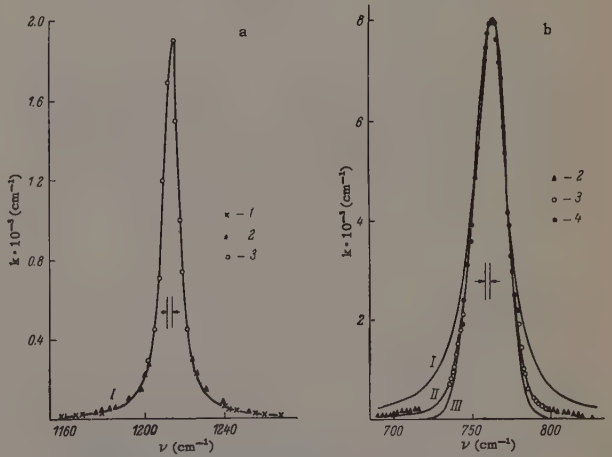

Fig. 1. Band contours of the ν_4 (a) and ν_5 (b) vibrations of liquid $CHCl_3$. Solid curves—theory: I—calculation according to formula (1), II—according to (3), III—according to (2); points—experimental data, obtained with cells of different thickness: 1—320 and 180 μ; 2—100 and 60 μ; 3—5.6 and 8.2 μ; 4—"effective" thickness,[16] $\Delta p_{eff.} = 0.73\ \mu$.

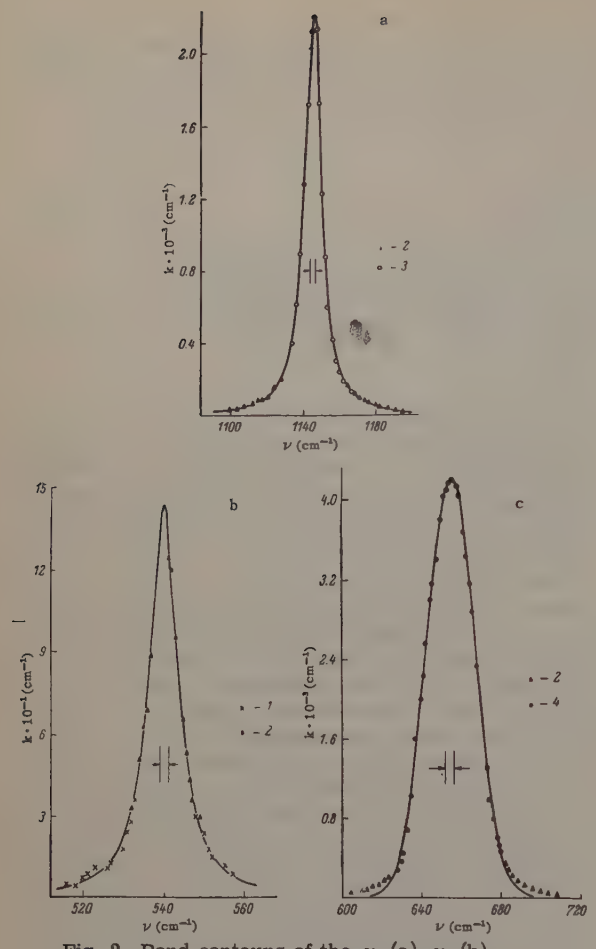

Fig. 2. Band contours of the ν_4 (a), ν_2 (b), and ν_5 (c) vibrations of liquid $CHBr_3$. Solid curves—theory: a and b—calculated according to formula (1), c—according to (2); points—experiment (cf. legend to Fig. 1).

width of the band, $\Delta\nu_s$ the spectral slit width), the measured curves for the distribution of the absorption coefficients do not differ appreciably from the true ones.[2,7,18] This circumstance allowed the experimentally obtained contours to be directly compared with the calculated ones according to the following formulas: dispersion,

$$K_d = \frac{K_{max}}{1 + \left(\frac{\nu - \nu_0}{\frac{G}{2}}\right)^2} \qquad (1)$$

and Gaussian,

$$K_G = K_{max} \exp\left\{-2.77\left(\frac{\nu - \nu_0}{G}\right)^2\right\}, \qquad (2)$$

where K_{max} and ν_0 are the absorption coefficient and frequency values corresponding to the band maximum. The results of the computations are shown in the figures by solid curves.

It is easy to see that the contours of the bands corresponding to the ν_2 and ν_4 vibrations of chloroform and bromoform are described with a high degree of accuracy by the dispersion formula (1). It is appropriate to mention here that the authors of refs. 2, 4, 7, and 8 consider the dispersion shape to be general for the overwhelming majority of vibrational absorption bands. However, according to our measurements, the shape of the vibration band differs substantially from the dispersion shape—in the case of bromoform it is almost Gaussian (Fig. 2c), while for chloroform it is significantly closer to the Gaussian (curve 3, Fig. 1b) than to the dispersion curve (curve 1, Fig. 1b), and is satisfactorily described by a linear combination of Eqs. (1) and (2), namely

$$K = \frac{10}{13} K_G + \frac{3}{13} K_d. \qquad (3)$$

We note that a Gaussian contour has also been observed for certain bands in refs. 1 and 19.

It is not without interest that, in our measurements the contours of the very intense bands approach the Gaussian shape. At present it is difficult to say to what extent this fact is general. It should be noted in any case that it is also observed in the spectrum of liquid CCl_4,[18] in which the most intense band, that of the ν_3 vibration, has a Gaussian shape, while the weaker combination frequencies are described by combinations similar to formula (3).

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HE EFFECT OF TEMPERATURE ON THE INFRARED SPECTRA OF ORGANO-SILICON COMPOUNDS

I. Crystalline Hexaethyldisiloxane

I. Crystalline Hexaethyldisiloxane

O. V. Vakulenko, G. G. Kirei and M. P. Lisitsa (pp. 196-202)

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The effect of temperature and of the liquid crystal phase transition on the structure and intensity of the vibrational absorption bands of hexaethyldisiloxane has been investigated. A comparison between the experimental results and theory has been made.

RODUCTION

Previously we have investigated the temperature ndence of vibrational absorption band intensities of ively simple molecules in the gas, liquid, and solid es. Analogous investigations of complex molecules d be of substantial interest, as they might clarify the ence of temperature on the anharmonicities of vibra-, intermolecular interactions, and nature of the ex--phonon bonding. Silicon organic compounds belong is desired type of molecules.

Below is the discussion of the results of an investi-n of the temperature dependence of the intensities of of the vibrational absorption bands of crystalline ethyldisiloxane. The overtone and combination bands e not studied extensively. Considerable attention was to the effect of the liquid-crystal phase transition ne intensity, position, and structure of the absorption s.

ERIMENTAL METHOD

All measurements were performed on an IKS-6 spec-hotometer. The cryostat and the hermetically ed cell have been described previously in refs. 1 and espectively. The cell was filled under vacuum thus imizing loss of liquid and preventing breaking of the r during the experiments. The temperature was lated to ± 2-3° C.

The thickness of the absorbing layer was determined the thickness of the spacers which were chosen such the central part of an absorption band could be meas-with the greatest possible precision. In calculating absorptivity for a solid phase, it was assumed that hickness was unaffected by crystallization. The rptivities of solid hexaethyldisiloxane were not cor-ed for change in density with variation in tempera-because of the insignificance of the correction.

ERIMENTAL RESULTS AND DISCUSSION

(a) Variation in Frequencies, Structures, and Inten-s of Bands During the Liquid-Crystal Phase Transi-. The spectrum of hexaethyldisiloxane has been de-ibed previously.[3] We will use the frequency assign-t made in the foregoing paper in discussing our re-s presented in Figs. 1-6, concerning the effects of iation in the temperature. Each figure shows the ab-ption curve of the liquid at −65° C in order to illustrate the effect of the phase transition. The maximum temperature at which the absorption of crystalline hexaethyldisiloxane was measured was 1-2° lower than the melting point (~ −80° C). Since the vibrational band parameters of molecular compounds are, in general, weakly temperature-dependent, a difference of 17-20° can not cause an effect that would be appreciably larger than the experimental error. Hence all changes in intensity, shape, half-width, and position of the bands at the two foregoing temperatures are almost entirely determined by the change in the state of aggregation.

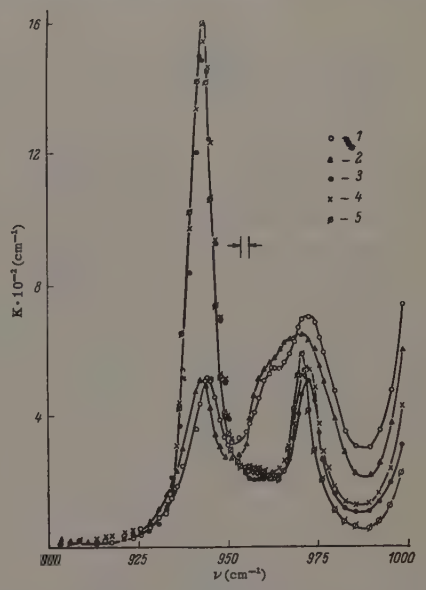

Fig. 1. The absorption of hexaethyldisiloxane in the region of C—C valence bond vibrations. State of aggregation and temperature (in ° C): 1—liquid (−65); 2—liquid (−160); 3—crystal (−80); 4—crystal (−120); 5—crystal (−163).

Let us note, first of all, the relatively small shift in the vibration frequencies* during the phase transition,

*In this paper the vibration frequencies quoted are for a temperature of 20° C. Hence the values could be different for lower temperatures.

and also the fact that the observed shifts occurred towards increased as well as decreased frequencies. The largest shifts were experienced by the ν_{as} vibrations of Si—O—Si and the ν_s of CH_3 (+25 and −20° C respectively).

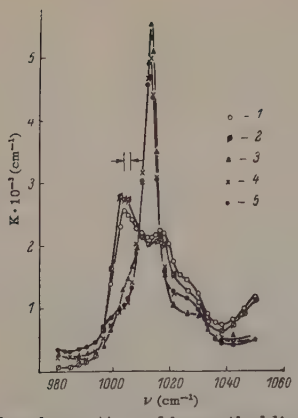

Fig. 2. The absorption of hexaethyldisiloxane in the 980-1050 cm^{-1} region. State of aggregation and temperature (in °C): 1—liquid (–65); 2—liquid (–120); 3—crystal (–80); 4—crystal (–120); 5—crystal (–163).

The positions of the remaining bands were either unaffected or were shifted very little. This result is trivial and is observed in the case of all molecular compounds. It indicates that the effect of intermolecular interactions on the frequencies of intramolecular vibrations is very weak.*

*It must be remembered that "weak" is a relative notion since some phenomena can be caused by weak interactions (for example, change in selection rules due to a phase transition).

The excessive shifts in the frequencies of the valence symmetrical vibration of the methyl group (2912 cm^{-1}) and the valence antisymmetrical vibration of the Si—O—Si group (1082 cm^{-1}) are easily explained. In the intermolecular interactions leading to the formation of a crystalline lattice the main role belongs to the peripheral C—H bonds and the central bonds of the group Si—O—Si. As a result of these interactions the charge of the former decreases while that of the latter increases, thus leading to the corresponding decrease and increase in the force constants and a concomitant decrease and increase in the corresponding vibration frequencies. Such a charge re-

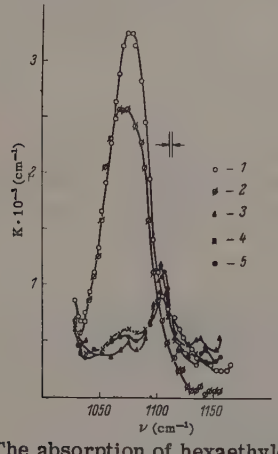

Fig. 3. The absorption of hexaethyldisiloxane in the region of ν_{as} vibrations of Si—O—Si. For state of aggregation and temperature see legend to Fig. 2.

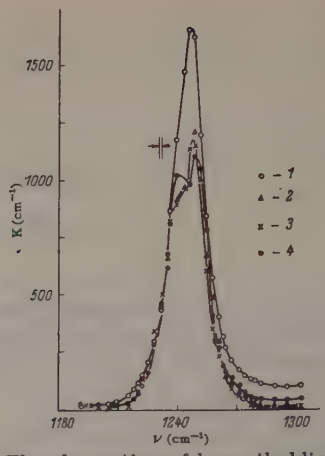

Fig. 4. The absorption of hexaethyldisiloxane in the region of δ_s vibrations of $CH_3(CH_2)$. State of aggregation and temperature (in °C): 1—liquid (–65); 2—crystal (–80); 3—crystal (–120); 4—crystal (–170).

distribution is explained by the great electronic similarity between the Si—O and the C—H bonds.

As can be seen from the accompanying figures, the liquid-crystal phase transition leads to a substantial decrease of the intensities of the fundamental vibrations, in particular the bands at 970 and 1082 cm^{-1}. Only the 946 cm^{-1} band is the exception whose intensity is appreciably increased. The intensities of the two unidentified bands at 1004 and 1017 cm^{-1} remain unchanged (Fig. 2) (the band areas for the liquid and solid are equal within the experimental error). Similarly, the intensities of the majority of bands due to the combination and overtone vibrations are also unchanged (Fig. 6).

The decrease in the intensity of the vibrations in the solid phase relative to the liquid phase is due not so much to the "freezing-out" of the rotational degrees of freedom as to the much more strict fulfillment of the selection rules. It is quite natural to assume that due to the absence of long-range order and the fact that any con-

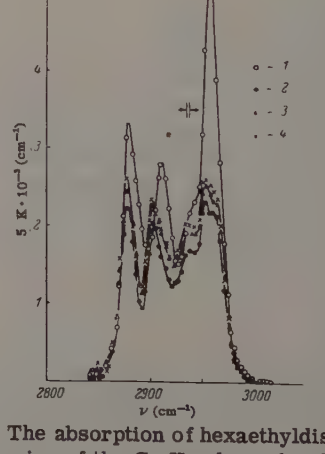

Fig. 5. The absorption of hexaethyldisiloxane in the region of the C—H valence bond vibrations. State of aggregation and temperature (in °C): 1—liquid (–65); 2—crystal (–80); 3—crystal (–130); 4—crystal (–180).

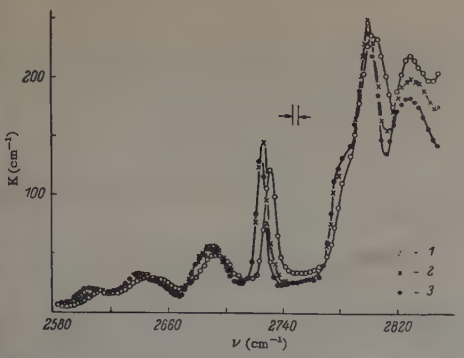

Fig. 6. The absorption of hexaethyldisiloxane in the region of the combination and overtone vibrations. State of aggregation and temperature (in °C): 1—liquid (–65); 2—crystal (–120) 3—crystal (–192).

ration of the force field acting on the molecule is sible, all the intramolecular vibrations including the bination and overtones are allowed in the liquid state. natural that the intensity of the vibrations forbidden isolated molecules can be small but not zero as in the of crystals.

Cases of increase in intensity during the liquid-crystphase transition are relatively rare. In our investigathere was only one definite instance. It can be exned by an increase in the dipole moment of the C—C due to a decrease in the dipole moments of the cenand peripheral bonds of the molecule. This explanawas substantiated by the decrease in the intensity of corresponding bands of crystalline hexaethyldisiloxane, ticularly in the case of the ν_{as} vibration of Si—O—Si.

The redistribution of charge between the C—H and O bonds on one hand and the C—C bonds on the other be caused not only by variation in the intermolecular e field determined by the appearance of long-range er but also by deformations of the molecule (for exole variation in the Si—O—Si angle). Hence x-ray or tron diffraction analysis of the structure of crysine hexaethyldisiloxane would be very desirable.

The overlapping of separate maxima (Figs. 2, 5, 6) the appearance of structure in the solid phase (Figs. , 5) hinder the determination of the true contours of absorption bands. Hence without considering the pe of the bands we will examine only the observed iations in structure. In the case of combination and rtone vibrations no similar changes took place (Fig. In the case of the fundamental vibrations, crystallilion led to a partial increase in the complexity of the ucture (Figs. 3-5). The exception was the triplet in region 1000-1040 cm^{-1} (Fig. 2) which was transmed into a very sharp band with barely noticeable ellites on either side—a possible explanation of the appearance of one of the two most intense bands of triplet lies in the foregoing analysis. The appeare of two almost equidistant satellites to the ν_{as} band Si—O—Si (Fig. 3) can not be explained either by a vydov[4] or a Bethe[5] type of splitting. The most acceptse explanation follows from the theory proposed retly in ref. 6. If the vibrational band be treated as the earance of a Frenkel exciton, then under the condin of positive effective mass of the latter it is possible expect the appearance of two additional maxima on ner side of the main band. The experimental realizan of this consequence of the foregoing theory is possible only if the parameter determining the temperature dependence of the vibrational band depends in a complex manner on the frequency of the incident radiation. It is impossible to establish at present how often such a phenomenon would be observed since the theory was constructed for cubic lattices, and even in this simplest case it is very hard to analyze the frequency dependence of the above-mentioned parameter. Since hexaethyldisiloxane does not crystallize into a cubic lattice the problem is even more complicated.

Of all the bands investigated only two were split into two components during the phase transition. One of the two bands belonged to the symmetric deformation vibration δ_s of the group $CH_3(CH_2)$, the other to the valence antisymmetric vibration ν_{as} of the methyl group (the appearance of a long wavelength component of the latter band is due to the general narrowing of the band and better resolution of the band belonging to the antisymmetric valence vibration of the CH_2 group). Since the deformation vibration is not degenerate and the molecules in the crystalline lattice are not associated (as evidenced by the absence of any association in the liquid phase), then this splitting must be due to resonance interaction between differently oriented molecules in the crystalline lattice. It is harder to determine the nature of the splitting of the twofold degenerate vibration of the CH_3 group. Here either the degeneracy can be removed or the Davydov type splitting can occur. The former is the most probable in the case where the CH_3 group is examined separately from the main part of the molecule and is assigned the C_{3v} point group. If the vibration is examined from a more general point of view, assuming that the symmetry of the molecule is C_{2v},[3] then we will have random degeneracy instead of true degeneracy. Random degeneracy usually persists (with the exception of cases corresponding to Fermi resonance) and hence we can interpret only one band irrespective of the number of bands coinciding in their frequencies.

(b) The Effect of Temperature on the Intensities. The main characteristic of the vibrational bands of crystalline hexaethyldisiloxane is the weak temperature dependence of their intensities. In the case of simple molecular compounds the effect of temperature on the band intensities is in general much stronger,[2] with a substantial range of temperature factors for individual vibrations. Analysis of the temperature curves shows that with increase in temperature the general tendency is towards a decrease in the absorptivity. This is true of the 946 cm^{-1} band (Fig. 1), the long wavelength component of the δ_s vibration of the $CH_3(CH_2)$ group (Fig. 4), and the whole group of C—H valence vibrations (Fig. 5). A small increase in absorptivity at the band maximum was observed in the case of the 1017 cm^{-1} band (Fig. 2), in that of the short wavelength component of the δ_s vibration of the $CH_3(CH_2)$ group (Fig. 4), and that of the combination vibration at 2832 cm^{-1} (Fig. 6). In the remainder of cases it was not even possible to speak of any temperature dependence.

The increase in the intensity of the absorption band at its maximum and in the half-width of the band is explained qualitatively by A. S. Davydov's theory[4] which was used previously by one of us to interpret the temperature dependence of the vibrational absorption band intensities of crystalline chloroform and bromoform.[2] It is impossible to explain the negative temperature effect using this theory without making additional assumptions. However the theory of V. L. Strizhnevskii[6] developed for the case of weak exciton-phonon interaction can be used

to explain the negative temperature effect.

This theory, assuming the independence of the complex polarizability of the crystal from the quasi-impulse of the exciton (space dispersion does not occur[7,8]), gives the following relation for the temperature dependence κ of the absorption

$$\varkappa = \frac{\frac{agT}{4\omega\sqrt{n}}}{(\omega_0-\omega)^2+\frac{g^2T^2}{4}}, \quad (1)$$

where ω_0 is the circular frequency corresponding to the absorption maximum,* ω is the actual frequency, n is the refractive index in the region of transmittancy, g is a parameter determining the band contour and depending on ω, and

$$a = 4\pi V |P_f(0)|^2 \frac{\omega_0}{\hbar}.$$

*In general this is true only in the case where the relative disposition of the dispersion curve and the absorption curve is the same as in the case of the harmonic oscillator.

Here V is the volume of the unit cell of the crystal, $P_f(0)$ is the matrix element of the dipole moment of a unit volume corresponding to the phototransition. Thus in order to calculate κ it is necessary to know ω_0, α, and g and also n at every temperature.

Let us first analyze the expected dependence of α_{max}. In this case $\omega_0 = \omega$ and instead of (1) we will have

$$\varkappa_{max} = \frac{4\pi V |P_f(0)|^2}{\hbar g T\sqrt{n}}. \quad (2)$$

Since V, $P_f(0)$ and g do not depend on T and the temperature dependence of n is of a smaller order of magnitude than α, then

$$\varkappa_{max} = \frac{A}{T}, \quad (2')$$

where

$$A = \frac{4\pi V |P_f(0)|^2}{\hbar g\sqrt{n}}$$

is a constant. Thus the absorption at the band maximum must decrease with the increase in temperature. It is easily seen that the same relationship holds not only at the band maximum but also at least within the confines of the band half-width, i.e., where the following inequality is fulfilled

$$|\omega_0-\omega| \ll \frac{gT}{2}. \quad (3)$$

These conclusions are qualitatively supported by the observed temperature dependence of the absorption bands of hexaethyldisiloxane enumerated above, the bands of the combination $\nu_1+\nu_3$ vibrations of and the $2\nu_3$ overtone of carbon tetrabromide,[9] and the long wavelength components of the doublets corresponding to the ν_5 vibrations of chloroform and bromoform.[2]

Quite a different situation occurs for the wings of the bands where the following inequality holds true

$$|\omega_0-\omega| \gg \frac{gT}{2}, \quad (4)$$

leading to a qualitatively different temperature dependence

$$\varkappa = \frac{4\pi V |P_f(0)|^2 \frac{\omega_0}{\hbar} gT}{(\omega_0-\omega)^2}. \quad (5)$$

Taking into consideration the foregoing limitations, Eq. (5) can be rewritten as

$$\varkappa = B\frac{T}{(\omega_0-\omega)^2}, \quad \left(B = \frac{1}{\hbar}4\pi V |P_f(0)|^2 \omega_0 g\right). \quad (5')$$

Equation (5′) shows that κ would increase with temperature, that it would be symmetrical relative to the maximum and that it would decrease on moving away from the maximum.

In general the experimental results do not agree with these predictions. Hence the impression can be created that in this respect the theory does not agree with experiment. However such a conclusion would be too hasty. First of all the investigated bands have a small temperature dependence; secondly, at relatively high temperatures the rate of increase at the wings should decrease (saturation effect) due to the decrease in the inequality (4). Thirdly, the absorption at the wings was measured with less precision and because of that a small increase in κ could have been missed. All this leads us to assert that at present the available experimental results do not contradict the theory.

In conclusion it is pertinent to examine our results on the supercooling of hexaethyldisiloxane. Figures 1-3 show the curves for the liquid phase at −65°C and for the supercooled liquid phase at −160°C (Fig. 1) and at −120°C (Figs. 2, 3). Notwithstanding the fact that the maximum supercooling was as large as 100°, no substantial changes in the structure of the absorption curves were observed. The only noticeable change was the decrease in the intensity of the ν_{as} vibration of Si—O—Si (Fig. 3). The effect of temperature on the spectrum of liquid hexaethyldisiloxane will be the subject of a future communication.

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EVIDENCE FOR HYDROGEN BONDING IN THE INFRARED SPECTRA OF CRYSTALLINE LITHIUM HYDROXIDES

A. I. Stekhanov and E. A. Popova (pp. 203-206)

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The infrared absorption spectra of hydrated and anhydrous lithium hydroxides and their deuterated analogs were measured in the region of the OH and OD valence vibrations. A broad intense band was observed in the spectra of the crystalline hydrates indicating the existence of a relatively short hydrogen bond in the crystals.

The study of the vibrational spectra of crystalline ates is of great interest in the investigations of hy- n bonding. At the same time it is the crystals contain relatively short hydrogen bonds that are cularly important and that are hard to find. In this ction the structure of the crystalline hydrate of m hydroxide presents a particularly interesting em.

The structure of $LiOH \cdot H_2O$ is sufficiently well known. rding to the results of references 1 and 2 it should in a hydrogen bond 2.66 A long. However the Raman ral investigations of Landsberg and Baryshanskaya,[3] lso of Phillips,[4] have detected only a single narrow t 3560 cm^{-1} corresponding, apparently, to the va- vibration of a free OH group. The absence from pectra of bands characteristic of a hydrogen-bonded roup contradicted the results of the structural in- gations. Hence further investigation of the vibra- spectra of $LiOH \cdot H_2O$ was important from the point w of a more accurate knowledge of the crystalline ture of hydrated lithium hydroxide.

The present paper is the report of a detailed investi- n of the infrared absorption spectra of crystalline ates of lithium oxide, anhydrous lithium hydroxide, heir deuterium analogs.

The absorption spectra were investigated using an 2 infrared spectrometer with a fluorite prism. The les investigated were monocrystals and thin films e hydroxides. A special vacuum cell was used for reparation of the films and the measurement of spec- t room and low temperatures. A thin film of lithium sited on a fluorite window in the foregoing cell re- i with the vapors of light or heavy (99.8%) water ing $LiOH \cdot H_2O$ or $LiOD \cdot D_2O$.

Direct reaction between metallic lithium and liquid r was also used to prepare the crystalline hydrates hium oxide. The infrared absorption spectra of crys- of $LiOH \cdot H_2O$ and $LiOD \cdot D_2O$ thus prepared were in- igated using organic oils as immersion liquids. The r method gave somewhat better results in the inves- ion of absorption spectra at room temperature. The drous hydroxides were prepared from $LiOH \cdot H_2O$ $LiOD \cdot D_2O$ through lengthy drying over phosphoric rdride under continuous evacuation.

Figure 1, curve a shows the absorption spectrum of rdrous lithium hydroxide in the OH valence vibration on measured at 300° K. It can be seen that the spec- n of crystalline LiOH exhibits a very narrow and p absorption band at 3676 cm^{-1}. The same narrow is observed at 2717 cm^{-1} in the spectrum of the y hydroxide (Fig. 2, curve a).

The absorption spectrum of the crystalline hydrate

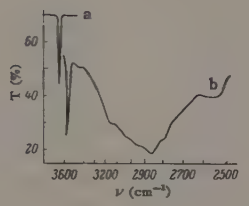

Fig. 1

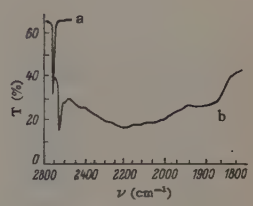

Fig. 2

Fig. 1. Infrared absorption spectra of LiOH (curve a) and $LiOH \cdot H_2O$ (curve b).
Fig. 2. Infrared absorption spectra of LiOD (curve a) and $LiOD \cdot D_2O$ (curve b).

$LiOH \cdot H_2O$ at 300° K is shown in Fig. 1, curve b. Apart from the sharp absorption band at 3570 cm^{-1} an intense band is observed, stretching from 2470 to 3500 cm^{-1} with its maximum at 2865 cm^{-1}. This band also exhibits subsidiary maxima at 3440, 3150, 2950, and 2800 cm^{-1} whose presence indicates a complex structure. Moreover a distinct, broad maximum at 2570 cm^{-1} is observed on the long wavelength side of the band.

Lowering of the temperature to 77° K leads to a shift of the whole spectrum towards lower frequencies. In this case the narrow band is at 3545 cm^{-1} while the maximum of the broad band is at about 2830 cm^{-1}.

The absorption spectrum of $LiOD \cdot D_2O$ is shown in Fig. 2, curve b. It is very similar to the spectrum of $LiOH \cdot H_2O$. It exhibits a narrow line at 2638 cm^{-1} and a broad band with a main maximum at 2190 cm^{-1}. Just as in the case of $LiOH \cdot H_2O$ the OD vibration band has a complex structure. At its long wavelength edge a broad maximum at 1850 cm^{-1} is also observed.

Let us examine the results obtained so far. The existence of a single sharp band at a frequency characteristic of free OH and OD vibrations in the spectra of the hydroxides LiOH and LiOD shows that hydrogen bonding in the crystals of the two hydroxides must be very weak. These results are in agreement with the crystallographic results,[5] according to which the minimum distance between the oxygen atoms of the hydroxyl groups in the lattice of LiOH is not less than 3.05 A.

The striking fact in the spectra of $LiOH \cdot H_2O$ and $LiOD \cdot D_2O$ is the appearance of a broad band strongly shifted to lower frequencies indicating the presence of strong hydrogen bonding in the two crystalline hydrates.

The possibility of the existence of a relatively short hydrogen bond in $LiOH \cdot H_2O$ has been pointed out previously.[1,2] According to the results of x-ray structural analysis, $LiOH \cdot H_2O$ belongs to the monoclinic system, has a C_{2h}^3 symmetry, and contains four molecules in its

elementary cell. The crystalline lattice, as can be seen from Fig. 3, consists of slightly distorted tetrahedra containing lithium atoms in their centers. Two opposed apices of each tetrahedron are formed by the hydroxyl ions and the others are formed by two water molecules. The distances between the oxygen atoms inside each tetrahedron are 2.99, 3.19, and 3.34 A. The distance between the water oxygen atoms and the hydroxyls of the neighboring tetrahedra is 2.68 A. According to the recent more accurate results[2] which substantiated, in general, the structure proposed in ref. 1, this distance is 2.66 A. Such a short distance must certainly lead to the formation of a strong hydrogen bond in the crystal of $LiOH \cdot H_2O$. Also a weak hydrogen bond should be formed in each tetrahedron between the hydroxyls 2.99 A apart. Thus the results of our spectroscopic investigation are in complete agreement with the results of x-ray analysis concerning the presence of a relatively short hydrogen bond in the crystalline hydrate $LiOH \cdot H_2O$.

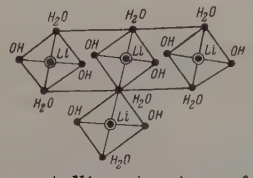

Fig. 3. The crystalline structure of $LiOH \cdot H_2O$. Projection on the (010) plane.

It seems surprising that the broad OH vibration band observed by us in the infrared and due to a hydrogen bond 2.66 A long has not been found in the Raman spectra of $LiOH \cdot H_2O$.[3,4] Since the Raman spectral investigations used powdered samples, we propose that the large amount of scattered radiation obscured the very broad OH vibration band.

In investigating the infrared absorption spectra of $LiOH \cdot H_2O$ it was noted that the broad OH vibration band was much weaker than the corresponding bands in the spectra of gypsum, boric acid, ice, and certain other crystals. It is possible that the intensity of the OH vibration band depends on the length of the hydrogen bond. Indeed the hydrogen bond in the foregoing crystalline hydrates is at least 2.7 A long, while in the case of $LiOH \cdot H_2O$ it is considerably shorter than 2.66 A. It is important to note in relation to the foregoing that the OH vibration bands in crystals with very short hydrogen bonds (about 2.59 A in seignette salt, dihydrogen phosphates of sodium, ammonium, potassium, etc.) are either very weak,[6] or do not appear at all.[7] We consider that an investigation of the intensity of the OH vibration band would be of undoubted interest.

The observed complex structure of the broad OH vibration band in the spectrum of $LiOH \cdot H_2O$ can be interpreted on the basis of a double potential minimum for the proton in the hydrogen bond. At the same time it must be kept in mind that combination frequencies can occur in this spectral region, due to the interaction of the OH vibrations with the vibrations of the hydrogen bond itself.

The appearance of the broad maximum on the long wavelength side of the OH vibration band can be due to the interaction of the deformation OH vibrations with the orientational vibrations of the water molecules and also with the vibrations of the crystalline lattice. The frequencies of the deformation OH vibrations occur in the region 1600-1700 cm^{-1} and the frequencies of the orientational vibrations of water at 700-800 cm^{-1}.

The existence in the spectra of the crystalline hydrates of a narrow band at 3570 cm^{-1} for $LiOH \cdot H_2O$ and at 2638 cm^{-1} for $LiOD \cdot D_2O$, shows that this band belongs to the vibrations of the weakly hydrogen-bonded hydroxyl groups (3A apart) inside each tetrahedron.

It must be noted that in our investigations of the spectra of crystalline hydrates, the ratio of the frequencies ν_{OH}/ν_{OD} of the narrow lines was 1.35, i.e., considerably less than 1.41, the ratio of the masses only. This fact illustrates the considerable anharmonicity of the vibration of the OH group in the investigated crystals.

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THE EFFECT OF FOREIGN GASES ON THE ABSORPTION OF INFRARED RADIATION BY WATER VAPOR

K. P. Vasilevskii (pp. 207-215)

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The effect of various foreign gases (Ar, N_2, air, CO_2) on the total absorption of infrared radiation by water vapor was investigated using a high resolution spectrometer and a multiple-pass cell. The absorption was caused by the single rotational line 4025.4 cm^{-1} and by a group of 9 lines in the region 3970-3978 cm^{-1}. The integral intensity ("strength") and half-width of the line 4025.4 cm^{-1} were determined. Values of 12.7, 4.9, 5.5, 5.6, and 6.8×10^{-8} cm, respectively, were obtained for the optical collision diameters of water molecules with each other and with molecules of argon, nitrogen, dry air, and carbon dioxide.

.. Starting with ref. 1 much attention has been paid perimental study of the absorption of heat radiation ater vapor. A short review dealing mainly with at-heric transmission in the infrared is given in refs. 1 3. Apparatus and results obtained on the humidity e upper layers of the atmosphere were described in 4 and 6; these data were obtained from the absorp-f solar infrared radiation by water vapor. A num-f recent papers[7] have dealt with the transmissivity tificial atmospheres. In all of these papers, however, r the total absorption due to several bands was in-gated, or the absorption was measured for separate s without resolving their structure. All effects re-to the fine structure of the band and the shape of ral lines were thus obliterated and the empirical ions obtained related the total absorption to para-rs such as the partial pressure of the vapor, the h of the path, the total pressure, and the temperature.

The advent of sensitive detectors of near infrared ation and the high resolution instruments based on have made it possible to perform more detailed stigations of the laws describing the absorption of ation by rotational-vibrational bands having fine cture.

Using a previously constructed high resolution vac- spectrometer and a multiple path cell[8] we investi-d the absorption of infrared radiation by water vapor e region of a single line and in the region of a group nes of the 2.7 μ band. The dependence of absorption ater vapor pressure and on the length of the path are n in ref. 9. Reference 10 gives data on the effect of ign gases (N_2, Ar, CO_2) on the total absorption of ra-on by the water vapor line at 4025.4 cm^{-1}.

In the present paper we will make a more thorough mination of the data on the effect of N_2, Ar, CO_2, and n absorption by the single water vapor line and we present the results of a similar investigation of a p of lines in the 2.7 μ band. The action of foreign s was studied both in order to simulate atmospheric itions and to obtain data on the efficiency of optical raction of various gas molecules with water mole-s.

2. Under the pressure and temperature conditions vailing in the lower layers of the atmosphere, the e of water vapor lines will be mainly determined by interaction forces which come into play in collisions ater molecules with each other and with molecules of r gases. In the visible and the near infrared range, re the line half-width is much smaller than the frequency ν_0 at the center of the line, the absorption coefficient k can be represented to a sufficiently good degree of approximation as a function of frequency by the Lorentz or dispersion equation[11]

$$k_\nu = \frac{S}{\pi} \cdot \frac{\gamma}{(\nu - \nu_0)^2 + \gamma^2}, \quad (1)$$

where $S = \int k_\nu d\nu$ is the integral intensity of the line.

At relatively low pressures, when the absorption mechanism remains unchanged

$$S = S^0 p_a, \quad (2)$$

where p_a is the partial pressure of the substance absorbing radiation. The half-width of the line γ is proportional to the frequency of intermolecular collision (following the Lorentz collision theory), and consequently will depend on the pressures of both the absorbing and the foreign gases.

According to definition, the integral absorption A of a line or a group of lines is equal to

$$A = \int \left(1 - \frac{I}{I_0}\right) d\nu,$$

where I_0 and I are the intensities of the incident and transmitted radiation respectively. Ladenburg and Reiche,[12] while examining A as a function of pressure and of the length of the path l, have found that for a single dispersion type line,

$$A = 2\pi\gamma f(x), \quad (3)$$

where $f(x) = xe^{-x}[I_0(ix) - iI_1(ix)]$. $I_0(ix)$ and $I_1(ix)$ are Bessel functions of the zero and first order respectively, and

$$x = \frac{Sl}{2\pi\gamma}. \quad (4)$$

3. In studying the absorption of radiation by water vapor in the region of the single line 4025.4 cm^{-1} in absence of foreign gases,[9] we found that for A values ranging from 0.07 to 0.9 cm^{-1} the following approximate equation is valid

$$A = 2\sqrt{S\gamma l}. \quad (5)$$

It was also demonstrated that

$$\gamma = \gamma^0 p_a, \quad (6)$$

where γ^0 is the half-width of the line for $p_a = 1$. Equation (5) is easily derived from Eq. (3) for $x \gg 1$.

The absorption of infrared radiation by the gas mix-

tures $H_2O + Ar$, $H_2O + N_2$, $H_2O + CO_2$, and H_2O + (dry) air has now been investigated by a similar method for a water vapor pressure of 0.009 atm (6.8 mm Hg), various total pressures of the mixture (up to 0.84 atm), and for path lengths of 8.8 to 160.8 meters. The experiments were performed at approximately 20°C. The foreign gas was introduced into the cell after first passing through a special drying arrangement. Figure 1 shows a region of the water vapor absorption spectrum which was obtained with a path length of 136.8 meters and shows the line investigated at various pressures of the foreign gas (CO_2).

Measurements of the line 4025.38 cm^{-1} (transition $6_{-2}-5_{-5}$) are plotted showing A as a function of $(p_a l)^{1/2}$. Figure 2 represents the addition of nitrogen and Fig. 3 represents the case of carbon dioxide. It follows from the given data that the integral absorption A can be represented by Eq. (5) between 0.07 and 0.9 cm^{-1}. In this case, however, the slope of curves 1-6 is proportional to $(p_a + \sigma_{ax}p_x)^{1/2}$. Consequently it can be assumed that

$$\gamma = \gamma^0 (p_a + \sigma_{ax} p_x), \qquad (7)$$

where σ_{ax} can be defined as the relative efficiency of optical collisions between water (a) and foreign gas (x) molecules.

A similar equation is also valid when argon and dry air are used as foreign gases. Deviations at values above $A > 0.9$ cm^{-1} are due to the overlapping of the investigated line with neighboring lines (see ref. 9). According to Eq. (3), the integral absorption of an isolated line for small values of the parameter $x = Sl/2\pi\gamma$ is

$$A = 2\pi\gamma x\left(1 - \frac{x}{2} + \frac{x^2}{4} - \ldots 1\right), \qquad (8)$$

and for $x < 1$

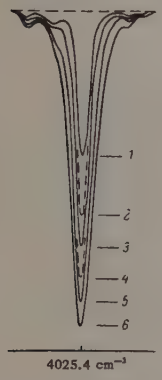

Fig. 1

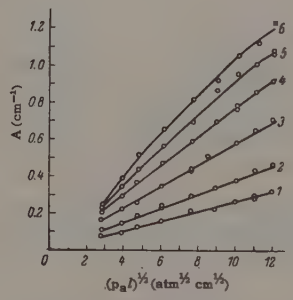

Fig. 2

Fig. 1. Region of the absorption spectrum of water vapor containing the line 4025.4 cm^{-1}. Curves 1-6 were obtained at a water vapor pressure of 0.009 atm and carbon dioxide pressures 0, 0.057, 0.188, 0.386, 0.596, and 0.832 atm respectively. Path length l = 136.8 meters.

Fig. 2. Integral absorption A in the water vapor line 4025.4 cm^{-1} as a function of the product $(p_a l)^{1/2}$ for various pressures of nitrogen. Water vapor pressure $p_a = 0.009$ atm. Nitrogen pressure p_x (in atm): curve 1—0; curve 2—0.057; curve 3—0.188; curve 4—0.386; curve 5—0.596; curve 6—0.832.

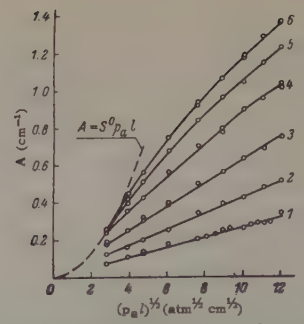

Fig. 3. Integral absorption A in the water vapor line 4025.4 cm^{-1} as a function of the product $(p_a l)^{1/2}$ for various pressures of carbon dioxide. Water vapor pressure p_a = 0.009 atm. Carbon dioxide pressure p_x (in atm): curve 1—0; curve 2—0.057; curve 3—0.188; curve 4—0.386; curve 5—0.596; curve 6—0.832.

$$A = 2\pi\gamma x = S^0 p_a l. \qquad (9)$$

The value of x for a pure absorbing gas (containing no foreign gases) can only be changed by a change in the path length l. The transition to the region of linear dependence of A as a function of the product $p_a l$ therefore requires a considerable decrease in path length, which is coupled with a decrease of the measured values of A and with a decrease in the accuracy of the measurements. x can be decreased without changing the path length by adding a foreign gas to the cell. This method of transition to the region of linear dependence of A on $p_a l$ is often used to determine the intensities (S^0) of lines or unresolved bands (see, for example, refs. 13 and 14).

It can be seen in Fig. 3 that for a minimum path length l = 880 cm and for large values of p_x (0.386, 0.596 and 0.832 atm) the integral absorption is independent of p_x and does not exceed 0.25 cm^{-1}.

Using Eq. (5) we obtain from curve 1, Fig. 2, for $p_x = 0$;

$$S^0\gamma^0 = 0.0195 \text{ cm}^{-3} \text{ atm}^{-2} \text{ (for t = 20°C)}.$$

It is easy to obtain an approximate value of S^0 from Eq. (9) and then determine the value of γ^0. Having determined the value of parameter x, one can estimate the magnitude of the correction terms in Eq. (8) and then find more accurate values of S^0 and γ^0 by the method of successive approximations. We obtained the following values for the water vapor line 4025.38 cm^{-1}:

$$S^0 = 0.039 \text{ cm}^{-2} \text{ atm}^{-1}, \quad \gamma^0 = 0.5 \text{ cm}^{-1} \text{ atm}^{-1}$$

(for t = 20°C)

In order to determine the line half-width at different pressures p_a and p_x, it is necessary to know the relative efficiencies of optical collisions σ_{ax}.

Using Eqs. (2) and (7), in the region where Eq. (5) can be applied, one can write

$$\frac{A^2}{4p_a l S^0\gamma^0} = p_a + \sigma_{ax} p_x. \qquad (10$$

The experimental data obtained are presented in Fig. 4 in a form which corresponds to Eq. (10). Values of σ_{ax} obtained from the slope of curves 1-4 are listed in the second column of Table 1.

Values of optical diameters for collisions of absorbing molecules among themselves (d_{aa}) and with molecule

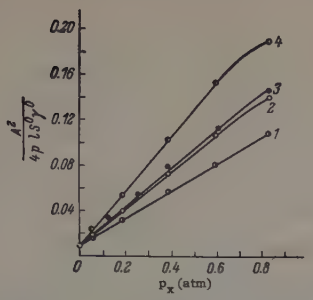

Fig. 4. Values of $A^2/4p_a l S^0 \gamma^0$ for the water vapor line 4025.4 cm^{-1} as a function of the pressure of foreign gases p_x. Curve 1—argon; curve 2—nitrogen; curve 3—air (dry); curve 4—carbon dioxide.

oreign gases (d_{ax}) can easily be obtained from the wn equation for the half-width of a line (see, for exple, ref. 15)

$$\gamma = \frac{1}{2c}\left[\sqrt{2}\, N_a v_a d_{aa}^2 + N_x (v_a^2 + v_x^2)^{1/2} d_{ax}^2\right]. \qquad (11)$$

ere N_a and N_x are the numbers of molecules per cm^3 the absorbing and foreign gases at pressures p_a and respectively, v_a and v_x are the relative velocities of liding molecules, and c is the velocity of light.

Taking account of Eq. (7), we obtain

$$d_{ax}^2 = \sigma_{ax}\gamma^0 \frac{2cp_x}{N_x}\left[\frac{m_a m_x}{2kT(m_a + m_x)}\right]^{1/2} \qquad (12)$$

d

$$d_{aa}^2 = \gamma^0 \frac{2cp_a}{N_a}\left(\frac{m_a}{4kT}\right)^{1/2}. \qquad (13)$$

Absolute values of the optical diameters of collins of water molecules among themselves and with gon, nitrogen, dry air, and carbon dioxide molecules, ained from the line investigated with the help of Eqs. ?) and (13), are shown in the third column of Table 1.

Table 1. Value of Relative Efficiencies and Absolute Optical Collision Diameters for Molecules of the System "Water-x"

x	σ_{H_2O-x}	$d_{H_2O-x} \cdot 10^8$ (в см)		
		Line 5_{-5}—6_{-6} in band ν_3	Line 5_{-1}—6_{-5} at 0.744 cm^{-1}	Gas-kinetic diameter (from ref. 17)
H_2O	1	12.7	12.2	2.53
Ar	0.123	4.9	—	3.09
N_2	0.165	5.5	—	3.14
Air	0.170	5.6	5.6	3.5
CO_2	0.239	6.8	—	3.56

The d_{ax} values which we obtained for the H_2O line $''_3 = 0$, $J''_\tau = 5_{-5} \rightarrow v'_3 = 1$, $J'_\tau = 6_{-2}$) are very close to vals shown in the fourth column of Table 1 for $d_{H_2O-H_2O}$ d d_{H_2O-air} for the line 5_{-1}—6_{-5} in the microwave region the spectrum (0.744 cm^{-1}) derived from data of ref. 16. should be pointed out that the optical collision diameters the system H_2O-x are larger than the gas-kinetic colsion diameters (especially in the case of H_2O-H_2O collions).

5. Let us examine the absorption caused by a group of lines which are components of the vibrational-rotational band. Recently obtained high resolution infrared spectra of water vapor[18–23] display an extremely complicated band structure.

A theoretical calculation of the amount of radiation absorbed in such bands is very complicated and can only be achieved by considerable schematization of the band structure. Several schematic models of bands are discussed in a book by Kondrat'ev.[24] In a number of cases, however, the lines forming a group are fairly far apart (the distance between the lines is considerably greater than their width). In this case the integral absorption A_n, caused by a group of n such lines, must be determined by direct summation, that is,

$$A_n = \sum_{i=1}^{n} A_i,$$

where A_i is the integral absorption due to the i-th line.

As in a preceding paper,[9] we have investigated the absorption due to a group of 9 lines of various intensities, located at various distances from each other in the 3970-3978 cm^{-1} region and belonging to the ν_1 and ν_3 bands. The lines in question are indicated by arrows in Fig. 5, which was obtained with a path length of 64.8 meters, a water vapor pressure of 0.009 atm and various pressures of the foreign gas (CO_2) (indicated in the description of the figure).

We had previously shown[9] that in the absence of foreign gases, the integral absorption by a group of lines is

$$A_n = 2p_a\sqrt{l}\sum_{i=1}^{n}\sqrt{S_i^{0}\gamma_i^{0}} \qquad (14)$$

for $A_n < 2.5$ cm^{-1}.

In view of the dependence of γ on p_a and p_x [Eq. (7)], it can be expected that the integral absorption of a group of lines in the presence of a foreign gas will be equal to

$$A_n = 2\sqrt{p_a l}\sum_{i=1}^{n}\sqrt{S_i^{0}\gamma_i^{0}(p_a + \sigma_i p_x)}. \qquad (15)$$

As shown by the experimental data presented in Fig. 6, a relationship of the type (15) is indeed observed for $A_n < 3.0$ cm^{-1}. Deviations from the given relationship which are observed at small path lengths and high foreign gas pressures (0.596 and 0.832 atm, are related, as in the case of a single line, to a decrease in the value of $x_i = S_i l/2\pi\gamma_i$ and to a transition to a region in which there is a linear dependence of the type

$$A_n = p_a l\sum_{i=1}^{n} S_i^{0}. \qquad (16)$$

Deviations for $A_n > 3$ cm^{-1} are due to a strong overlapping of lines,[9] causing experimental values of A_n to be smaller than the values calculated from Eq. (15). If the relative collision efficiencies σ_{ax} were equal for all lines comprising the group, it could be assumed that

$$A_n = 2\sqrt{p_a(p_a + \sigma_{ax}p_x)\, l}\cdot\sum_{i=1}^{n}\sqrt{S_i^{0}\gamma_i^{0}}.$$

Since

$$\sum_{i=1}^{n}\sqrt{S_i^{0}\gamma_i^{0}} = a = \text{const},$$

(ref. 9), a linear dependence of A_n^2 on p_x could be expected. Actually, as seen in Fig. 7, a function of this type is applicable to a single line, but does not describe the behavior of a group of lines when Ar, N_2, air, and

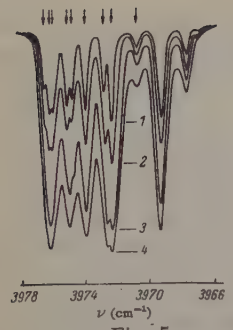

Fig. 5

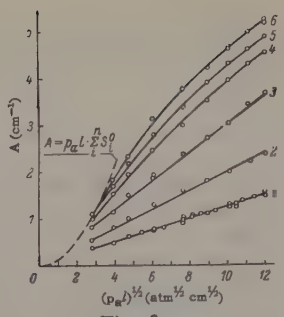

Fig. 6

Fig. 5. Region of the water vapor absorption spectrum containing the investigated group of 9 lines (marked by arrows). Curves 1-4 were obtained at a path length $l = 64.8$ meters, a water vapor pressure of $p_a = 0.009$ atm and carbon dioxide pressures p_x of 0.057, 0.386, and 0.832 atm, respectively.

Fig. 6. Integral absorption A of a group of water vapor lines as a function of the product $(p_a l)^{1/2}$ at various pressures of carbon dioxide. Water vapor pressure $p_a = 0.009$ atm. Carbon dioxide pressures (in atm): curve 1—0; curve 2—0.057; curve 3—0.188; curve 4—0.386; curve 5—0.596; curve 6—0.832.

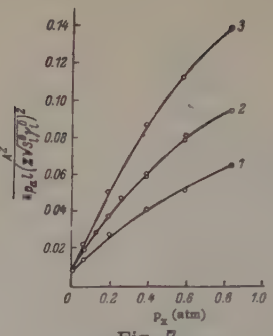

Fig. 7

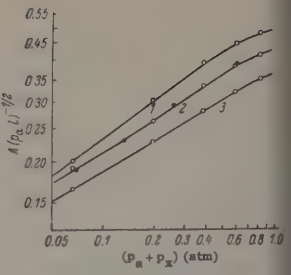

Fig. 8

Fig. 7 $\frac{A^2}{4p_a l}\left(\sum_{i=1}^{n}\sqrt{S_i^0\gamma_i^0}\right)^{-2}$ as a function of the pressure of foreign gases p_x for a group of water vapor lines. Curve 1—argon; curve 2—nitrogen (light points), air (dark points); curve 3—carbon dioxide.

Fig. 8. $\log(A/\sqrt{p_a l})$ as a function of $\log(p_a + p_x)$ for a group of water vapor lines at $p_a = 0.009$ atm and various pressures of foreign gases. Curve 1—carbon dioxide; curve 2—nitrogen (light points), air (dark points); curve 3—argon.

CO_2 are used as foreign gases (curves 1-4, respectively). This result is not surprising. This parameter σ_{ax} can actually be characterized as a ratio

$$\sigma_{ax} = \frac{\gamma_x^0}{\gamma_a^0}, \qquad (17)$$

where γ_x^0 is the half-width of the line in collisions of the absorbing molecules with molecules of the foreign gas x (for $p_x = 1$), and $\gamma_a^0 = \gamma^0$ is the half-width of the line caused by collisions between absorbing molecules (for $p_a = 1$ and $p_x = 0$).

Equal values of σ_{ax} for all lines of the group would mean the same dependence of γ_x^0 and γ_a^0 on the rotational quantum number J, and it is known that this is not the case.* The relative weight of different lines in the total absorption of the group of lines (band) varies with the pressure of the foreign gas because of the dependence of σ_{ax} on J, and consequently a group of lines in the region of validity of Eq. (15) (for $A_n < 3$ cm^{-1}) cannot be characterized by an averaged value of $\bar{\sigma}_{ax}$ which is independent of p_x. The character of the deviations of the functional dependence of A_n^2 on p_x from linearity is thus determined by the ratio of intensities of the lines comprising the group, and also by the ratio of the corresponding values of σ_i.

It is interesting to note in Fig. 7 that the broadening properties of nitrogen and dry air are equal within the accuracy of measurement for the given group of lines. A direct application of Eq. (15) to determine p_a values from measured values of A_n and known values of p_x requires a knowledge of $S_i^0\gamma_i^0$ and σ_i for each line in the group.

*Variation in γ_x^0/γ_a^0 as a function of J was observed experimentally in cases of broadening of rotational lines with increasing pressure of the absorbing gas and upon addition of foreign gases for the HCN band at approximately 1.038 μ[25] and for ground state bands of CO and DCl.[14]

6. The experiments indicated that the equations obtained in ref. 7 for "weak" ($A_n < 3$ cm^{-1}) and "strong" bands are valid for the A_n values investigated. In the case of $A_n < 3$ cm^{-1}, the equation for "weak" bands, using our definitions, has the form

$$A_n = b\sqrt{p_a l}\,(p_a + p_x)^k. \qquad (18)$$

Experimental data are shown in Fig. 8 in the form of a plot of $\log(A_n/\sqrt{p_a l})$ as a function of $\log(p_a + p_x)$. It can easily be seen that an empirical equation of the type of (18) is obeyed well for A_n values ranging from 0.5 to 3 cm^{-1}, leading to the values of b and k listed in Table 2

Table 2. Values of b and k

Foreign gas	b	k
Ar	0.368	0.29
N_2 or air	0.440	0.31
CO_2	0.542	0.37

Table 3. Values of Constants C, m, and n

Foreign gas	C	m	n
CO_2	—2.68	3.75	2.52
N_2 or air	—2.13	3.12	2.12
Ar	—3.28	3.38	1.75

Data on broadening of the group of lines by carbon dioxide are plotted in Fig. 9 for A_n as a function of $\log(p_a l)$. In this case the points corresponding to $A_n > 3$ cm^{-1} coincide with the family of parallel straight lines corresponding to various pressures of carbon dioxide. The straight line portions of the curves in Fig. 9 are accurately described by the equation for "strong" bands of the type

$$A_n = C + m\log(p_a l) + n\log(p_a + p_x). \qquad (19)$$

Values of the constants C, m, and n for different foreign gases are listed in Table 3.

Empirical equations (18) and (19), obtained by the authors of ref. 7 for bands as a whole, can thus be satis-

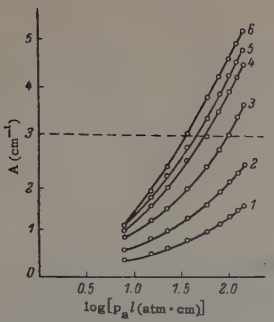

Fig. 9. Integral absorption A for a group of water vapor lines as a function of log ($p_a l$). Pressure of water vapor $p_a = 0.009$ atm; pressure of carbon dioxide p_x (in atm): curve 1—0; curve 2—0.057; curve 3—0.188; curve 4—0.386; curve 5—0.596; curve 6—0.832.

torily applied to single groups of lines also. Naturally, domain of validity of the given expressions and the ues of the constants will be different in every case.

We take the opportunity to express our gratitude to S. Neporent for his guidance in carrying out this work.

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CERTAIN REGULARITIES IN THE ELECTROLUMINESCENCE OF ZnS:Cu:Al PHOSPHORS WITH HIGH COPPER CONTENT

A. M. Bonch-Bruevich (pp. 216-222)

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A study has been made of the kinetics of the decrease in intensity of the green and blue luminescence pulses which accompany the turning on and off of the voltage applied to ZnS:Cu:Al phosphors. A study was also made of the steady state luminescence characteristics (the amplitudes of the luminescence pulses and the light sum emitted under the action of a pulsed voltage). It is shown that essential differences exist between the green and blue luminescence bands with regard to a number of the regularities observed.

1. It is known that the emission of ZnS:Cu:Al electroluminors contains two particularly pronounced bands, a green one with its maximum in the region of 520 mμ and a blue one with its maximum near 470 mμ. The ratio of the band intensities depends both on the copper concentration and on the technique of phosphor preparation.[1] The two bands have different luminescence characteristics. This results, in particular, in the dependence of luminescence color on the frequency of the applied voltage. A comparison of these characteristics may provide information concerning the relationship between centers of different types, and is essential for an understanding of the phosphor structure. Of particular interest is the behavior of the blue band when there is a decrease in the luminescence of the green band accompanying a variation in the electrical field in the case of fairly short voltage pulses.[2]

The main objects of our investigation were ZnS:Cu:Al electroluminors with a high concentration of copper (~0.2%).* We placed the phosphor mixed with transformer oil into a plane condenser with an interelectrode spacing of about 80 μ, one of the electrodes being transparent. The phosphor layer was separated from the electrodes by a polystyrene layer 20 μ thick. Electroluminescence was excited by rectangular voltage pulses. In our opinion this gives much more clear-cut results as regards changes in luminescence pulses (turn-on and turn-off pulses[2]) than do the harmonic voltage ("primary," "secondary," "in-phase," or 90-degree, 150-degree, 250-degree pulses referred to by different authors[3,4]). This shape of voltage pulse is also for studying the kinetics of luminescence. The voltage pulses were produced by generators which differed from those used in ref. 2 only by their ability to supply a somewhat larger voltage amplitude. We studied the turn-on and turn-off light pulses by means of a cathode ray tube oscillograph using a linear or an exponential sweep (the well-known "taumeter" method). The light filters placed in front of the photomultiplier (FEU-19) photocathode were chosen so that there was negligible overlapping of the green and blue regions transmitted. We studied the steady state luminescence characteristics and the kinetics of the decrease in luminescence of the light pulses accompanying voltage turn-on and turn-off; namely, the amplitudes of the light pulses and the light sum emitted under the action of a pulsed voltage. All measurements were carried out at room temperature. The notation used below is explained in Fig. 1, in which the turn-on and turn-off pulses are arbitrarily shown as being equal. For the phosphors studied, the turn-on light pulse was smaller than the turn-off pulse for both the green and blue bands, no matter which side of the condenser was used for observations.

*The electroluminors were kindly given us by F. M. Pekerman, to whom we express our sincere gratitude.

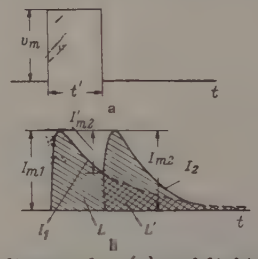

Fig. 1. Voltage pulse (a) and light pulses (b). v_m and t' represent the amplitude and duration, respectively, of the voltage pulse; I_1 and I_{m2} are the instantaneous values and the amplitude, respectively, of the turn-on light pulses; I_2, I_{m2}, and I'_{m2} are the corresponding quantities for the turn-off pulses; L is the light sum corresponding to one voltage pulse, and L' is the portion of the light sum of the turn-on pulse which corresponds to the time $t > t'$.

2. Observation of the kinetics of turn-on and turn-off light pulses* in the green and blue emission bands shows that the law of decay of the luminescence excited both at the application and the cutoff of the electrical field depends only slightly on the amplitude of the voltage pulses. (In our experiments the latter varied by a factor of about 2.5; this was accompanied by a change in luminescent intensity of almost two orders of magnitude.) This is illustrated in the graphs shown in Fig. 2, which represent the result of superposition of oscillograms of the corresponding light pulses obtained with an exponential sweep. In these experiments, the duration of the voltage pulses was chosen sufficiently large (500 μsec) so that at the instant the voltage is applied, the turn-off light pulse is practically completely extinguished. As seen from these

*A distinction between turn-on and turn-off light pulses is obviously meaningful only if $t' \neq T/2$. For $t' = T/2$, both pulses are equal. In our experiments we chose 10 μsec as the interval between voltage pulses and the maximum value $t' = 500$ μsec.

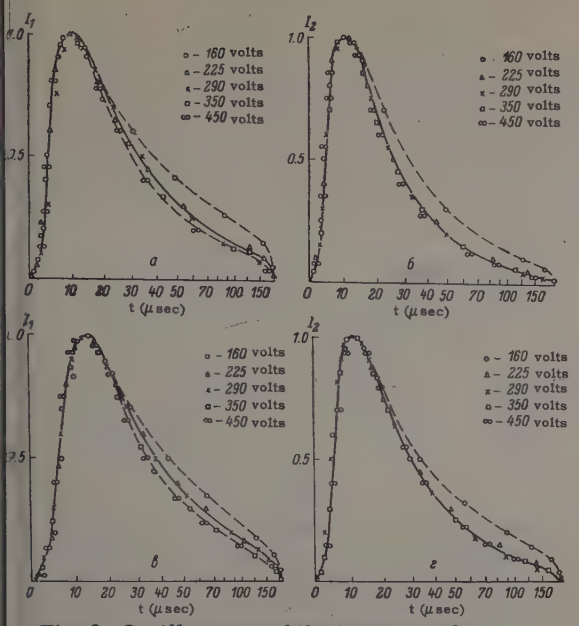

Fig. 2. Oscillograms of the turn-on and turn-off light pulses (I_1 and I_2, respectively) in the blue band (a and b) and the green band (c and d) for different values of v_m.

phs, a decrease in the voltage across the sample from to 225 volts has no effect on the kinetics of turn-off ut pulses in either spectral band. It only slightly ac- erates the rate of decay in the turn-on light pulses. n the amplitude of the voltage pulses is decreased l further, the rate of luminescence decay is somewhat wed down in all cases.

A variation in the duration of voltage pulses affects kinetics of luminescence decay somewhat differently. e decay kinetics of the turn-on pulse in the blue band iously change when t′ is varied, while the kinetics of turn-off pulses in the green band remain practically ariant up to t′ = 30 μsec. (See the graphs in Fig. 3.)

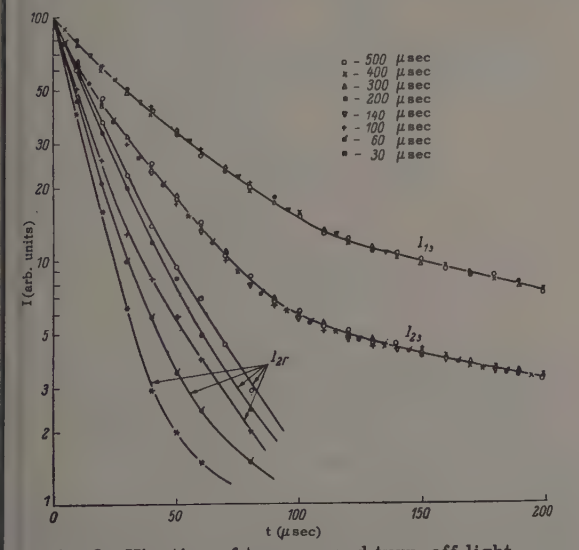

Fig. 3. Kinetics of turn-on and turn-off light pulses in the green and blue bands for different values of t′, the voltage pulse duration.

At the same time, the kinetics of luminescence decay of the turn-on light pulses is independent of the magnitude of t′ in the green as well as in the blue band. (This is natural as long as $T \gg t'$.) The laws for the decay of luminescent intensity are complex even though within fairly large ranges of brightness variation they may be approximated by functions of the type $I \sim e^{-t/\tau}$.

A study of the experimental data shows that the increase in the rate of decay of the turn-off light pulse in the blue band when the duration of voltage pulses is decreased cannot be explained by a simple superposition of the turn-off light pulse over part of the turn-on pulse corresponding to the time intervals $t > t'$. We might think therefore that if t′ is small and the turn-on pulse in the blue band does not have the time to decay completely, then there is a marked change in the rate of decay of the luminescence occurring when the voltage is cut off. On the other hand, the fact that $I_2 = f(t)$ is independent of t′ in the green band leads to the assumption that the turn-off light pulse in this band is not complicated by the superposition of the part of the turn-on pulse corresponding to the time $t > t'$. This can occur if the voltage cutoff is accompanied by a decrease of the turn-on luminescence in the green part of the spectrum.[2]

3. The emission light sum corresponding to one voltage pulse was determined by the electrical integration of signals taken off the photomultiplier load and by graphical integration of the oscillograms of the turn-on and turn-off light pulses. We found that for all phosphors investigated, the light sum remains practically unchanged for $500\ \mu\text{sec} > t' > 30\ \mu\text{sec}$. (See Fig. 4.) This may be interpreted as an indication that the light sum does not depend on t′ in either the turn-on pulse or the turn-off pulse; i.e., as an indication that the processes accompanied by the emission of blue light at voltage turn-on and turn-off occur independently.

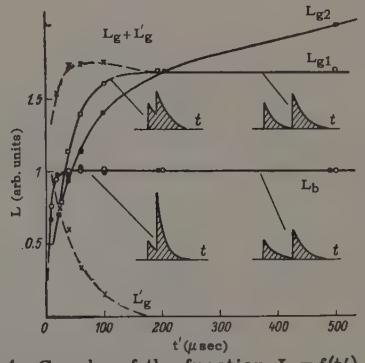

Fig. 4. Graphs of the function $L = f(t')$ for the blue and green bands.

The light sum in the green part of the spectrum is a function of the duration t′ of the voltage pulses. For one phosphor it decreases appreciably starting at $t' \sim 100$ μsec, while for another phosphor the decrease occurred even for long voltage pulses. (See Fig. 4.) This effect confirms the decrease in luminescence mentioned above. It is characteristic that if we combine the light sum of radiation in the green band with the light sum corresponding to the turn-on light pulse in the $t > t'$ range, this compensates for the decrease in the light sum observed in the range $t' < 100$ μsec (curve $L_g + L'_g$ in Fig. 4). The second light sum mentioned may be found by a graphic integration of the corresponding decay curve for the turn-on

light pulse observed in Fig. 1 at a large value of $t' - L_g$. A certain excess in the values of $L_g + L'_g$ over the value of L_g corresponding to long voltage pulses may be connected with the fact that in reality the decrease in luminescence requires a finite length of time, so that the true value of the light sum L'_g lost in this case is smaller than the quantity determined as shown in Fig. 1.

The graphs of Fig. 5 show the light sum corresponding to each voltage pulse as a function of the latter's amplitude. (This light sum is proportional to the luminescent intensity of the sample for a given repetition rate of the pulses.) In the blue band, this function is well represented by the relationship

$$L = Ae^{-\frac{B}{\sqrt{U_m}}}, \qquad (1)$$

where the coefficient B has a value of the order of 190 volts$^{1/2}$. In the range $t' > 30$ μsec, the value of the coefficient A (as well as that of B) is independent of the duration of the voltage pulses. It is interesting to note that the function $L = f(U_m)$ in the green band follows the same law with the same numerical value of the coefficient B. Furthermore, if the graphs corresponding to different values of t' are made to coincide at one point, they agree at all points. This corresponds to the functional dependence of the coefficient A on t' represented graphically by the curves $L_g = f(t')$ in Fig. 4 and varying somewhat from one phosphor to another.

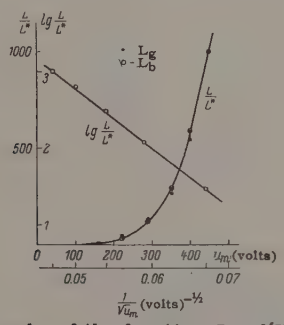

Fig. 5. Graphs of the function $L = f(U_m)$ for the blue and green bands. The spread in the values of L_g when t' varies from 40 to 500 μsec is shown for the green band.

4. If it is correct to assume that the turn-on luminescence decreases in the green band and that the turn-on and turn-off luminescence in the blue band are independent of each other, then the amplitude of the turn-off light pulses in the green band in the oscillograms should be measured from the zero line. In the blue band it should be measured from the level corresponding to the value of the emission from the sample at the instant $t = t'$ (I_{m2} and I'_{m2}, respectively, in Fig. 1). The amplitudes of the turn-on pulses should be measured from the zero line in both bands. The light pulse amplitudes determined in this manner are shown as functions of t' in the graphs of Fig. 6. The fact that the amplitudes of the turn-on pulses in the green band are practically invariant in the $t' > 30$ μsec range indicates the invariance of the excitation conditions of the corresponding centers when voltage is applied. The amplitude of the turn-off pulses in the green band is also independent of t'. (A slight increase in the magnitude of I_{m2} was observed for one of the phosphors in the $t' \sim 10$-40 μsec range. This might have been caused by a superposition of the turn-off pulse on the remaining luminescence of the turn-on pulse.) On the contrary, the amplitude of the turn-off pulses in the blue band increases systematically as t' decreases. This effect correlates well with the fact that the light sum in the blue band is constant at the same time that luminescence decays more rapidly as the voltage pulses become shorter. (Typical shapes of light pulses in the green and blue spectral regions are shown in Fig. 4 for different values of t'.)

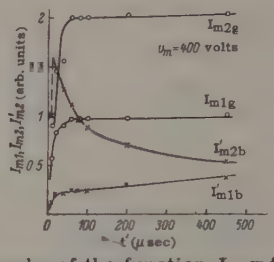

Fig. 6. Graphs of the function $I_m = f(t')$ for the green and blue bands.

As shown in the graph of Fig. 7, the amplitude of the turn-off light pulses depends on the voltage pulses according to a law analogous to (1):

$$I_m = A'e^{-\frac{B'}{\sqrt{U_m}}}. \qquad (2)$$

The variation in the amplitude of the turn-on pulses follows the same law in this band as in the blue band. Finally, the function $I_m = f(U_m)$ in the blue band follows the same law, while the curves corresponding to different values of t' are superposable. Thus a change in t' merely results in a change in scale of the corresponding curves, i.e., it amounts to a change in the quantity A' in Eq. (2). The character of this variation is represented by the curve $I'_{m2b} = f(U_m)$ in Fig. 6. It should be emphasized that the coefficient B' in Eq. (2) has the value ~200 volts$^{1/2}$. (For another phosphor we found the corresponding value $B' \sim 180$ volts$^{1/2}$.) Thus, for the phosphors studied, the value of B' practically coincides with the value of B in Eq. (1).

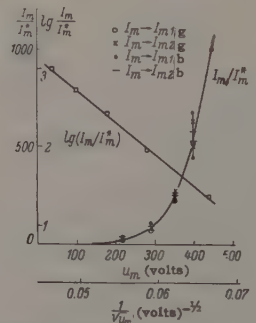

Fig. 7. Graphs of the function $I_m = f(v_m)$ for the green and blue bands. The vertical lines indicate the spread in the values of I_m when the duration of the voltage pulses varies from 40 to 500 μsec.

5. These experimental results indicate the existence of basic differences between several of the regularities observed in the green and blue bands, respectively. First there is a difference in the way the light sum stored in the two bands during a single voltage pulse depends on t',

duration of the pulse. There is also a difference in t t'-dependence of the amplitudes of the turn-off pulses ese bands. We do not feel that the fact that the lumi-cence excited when the voltage is applied decreases n the voltage is cut off contradicts the accepted me-nism of electroluminescence.[3-6] According to this me-nism, most of the luminescence is due to the return lectrons into the region of strongly ionized lumines-ce centers which is formed at the cathode. Actually, e voltage is cut off before essentially all of the lumi-cence centers have had time to recombine with elec-s, then an appreciable number of electrons will again removed from the region of ionization under the action e polarization field. The light sum emitted will rally be thus decreased. (Direct observation of the ease in luminescence in the form of an accelerated ay of a light pulse in the electroluminescent conden-is complicated by the fact that a light pulse arising nother crystal region is superimposed on the pulse h is dying out.

In our opinion, the essential point is that an analogous ct is not observed in the blue band of the phosphors lied. We may therefore consider that the emission of e centers is not controlled by electrons which, after rning to the region of strong ionization, may again be oved from it. At this time it is hard to find a reason it. However, in discussing various possibilities, we ld take two circumstances into consideration. First, fact that the law of luminescence decay is not exponen-probably indicates that the blue luminescence is not to isolated luminescence centers. Secondly, we should sider the change in the decay kinetics of the amplitude e turn-off light pulses when the voltage pulse dura-t' is varied, the light sum remaining constant. The iation in t' means a variation in the time interval be-en the formation of a region of strong ionization and return of electrons into it. The latter shows that a nge in the conditions of de-excitation of luminescence ters occurs before such de-excitation is accomplished, out any change in the number of centers.

The slight dependence of the luminescence kinetics he voltage applied to the sample is primarily due to fact that, at all voltages, the number of electrons ng part in the recombination luminescence is much ater than the number of ionized luminescence cen-s. Furthermore, the conditions necessary for the de-itation of centers when the electrons return to the region of strong ionization remain almost the same at all voltages.

Equation (1) for the light sum as a function of the voltage agrees with similar functions obtained earlier by other investigators, and is connected with the mechanism of center ionization.[3,5,7-9] The constancy of B when the voltage pulse duration t' is varied may be compared with the fact that this coefficient is independent of frequency when electroluminescence is excited by a harmonic voltage. Actually, this means that the ionization of the luminescence centers is completed very quickly. On the other hand, the dependence of A on t' in the green band is connected with the decrease in luminescence discussed above. The identity of the functions $I_m = f(U_m)$ and $L = f(U_m)$ (for a given voltage pulse duration) indicates that while the number of ionized luminescence centers increases with voltage, the probability of their de-excitation remains unchanged. This agrees in particular with the fact that the luminescence kinetics are independent of the amplitude of the voltage pulses.

The function $A' = f(t')$ in the blue band is connected with the changes already noted in the conditions of de-excitation of the blue emission centers when t' is varied. Since the reasons for this are not clear so far, we believe that special attention should be paid to the behavior of the coefficient A' in Eq. (2) under varying conditions of observation.

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THE ACTION OF AN ALTERNATING MAGNETIC FIELD ON THE PROPAGATION OF CIRCULARLY POLARIZED RADIATION IN MATTER

O. Ya. Savchenko (pp. 223-228)

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Starting with the Schrödinger equation, general formulas are obtained describing the change in the complex index of refraction for circularly polarized radiation in certain media, both within and without the anomalous absorption region, when these media are acted upon by an alternating magnetic field directed along the direction of propagation of the circularly polarized radiation.

The action of a constant magnetic field on the optical properties of a medium has been treated in detail in the literature.[1-3] The influence of an alternating field, however, has never been discussed, even though in this case unusual magneto-optic effects can be anticipated.

In what follows we shall consider the influence of an alternating magnetic field on the magnitude of the complex index of refraction for circularly polarized radiation being propagated in a gas in the direction of the magnetic field intensity vector.

In order to determine the refractive index of a gaseous medium, it is necessary to determine the character of the polarization of each individual molecule in the given radiation field. The polarization of a molecule is uniquely determined in the optical region by the form of the electronic wave function perturbed by the radiation field.[5]

Hence, in our treatment, our first task will be to obtain the wave function of an electron under the action of a magnetic field H(t) and, say, a right-circular wave traveling in the direction of the magnetic field intensity vector. When the molecular potential field V in which the electron moves depends only on the spherical coordinates r and θ (and is independent of the spherical coordinate ϕ), and the total spin moment of all the electrons is equal to zero, this wave function Ψ is found by solving the following Schrödinger equation[5]:

$$\Delta\Psi+\frac{2i\mu}{\hbar}\frac{\partial\Psi}{\partial t}-\frac{2\mu}{\hbar^2}V(r,\vartheta)\Psi+\frac{eH(t)}{i\hbar c}\frac{\partial\Psi}{\partial\varphi}-\frac{\mu Er\cos\vartheta}{i\hbar^2}[\exp i(\nu t+\varphi)+\exp i(-\nu t-\varphi)]\Psi=0. \quad (1)$$

Here μ and e are the electronic mass and charge, respectively, $2\pi\hbar$ is Planck's constant, c is the speed of light, E is the electric field intensity of the radiation, and $\nu/2\pi$ is the frequency of the radiation.

Far from the anomalous absorption region, Ψ can be approximated satisfactorily as the sum of two functions U_H and ω_H, where U_H is the wave function of an electron unperturbed by the radiation field. This function is defined by the equation:

$$\Delta U_H+\frac{2i\mu}{\hbar}\frac{\partial U_H}{\partial t}-\frac{2\mu}{\hbar^2}V(r,\vartheta)U_H+\frac{eH(t)}{i\hbar c}\frac{\partial U_H}{\partial\varphi}=0 \quad (2)$$

and can be written in the form

$$U_H=u(r,\vartheta)\exp\left(im\varphi-i\frac{W_k}{\hbar}t+\frac{emi}{2\mu c}\int^t H(\tau)\,d\tau,\right) \quad (3)$$

where m is an integer, and ω_H is defined by the equation

$$\Delta\omega_H+\frac{2i\mu}{\hbar}\frac{\partial\omega_H}{\partial t}-\frac{2\mu}{\hbar^2}V(r,\vartheta)\omega_H+\frac{eH}{i\hbar c}\frac{\partial\omega_H}{\partial\varphi}=\frac{\mu eEr\cos\vartheta}{\hbar^2}[\exp i(\nu t+\varphi)+\exp i(-\nu t-\varphi)]. \quad (4)$$

We write the solution of Eq. (4) in the form

$$\omega_H=\omega_H^+\exp\left[i(\nu t+\varphi)+im\varphi-i\frac{W_k}{\hbar}t+\frac{emi}{2\mu c}\int^t H(\tau)\,d\tau\right]+\omega_H^-\exp\left[-i(\nu t+\varphi)+im\varphi-i\frac{W_k}{\hbar}t+\frac{emi}{2\mu c}\int^t H(\tau)\,d\tau\right]. \quad (5)$$

Then the values of $\omega_H^{\pm}$ must satisfy the equation

$$\Delta\omega_H^{\pm}+\frac{2i\mu}{\hbar}\frac{\partial\omega_H^{\pm}}{\partial t}+\frac{m^2+1}{\sin^2\vartheta}\omega_H^{\pm}+\frac{2\mu}{\hbar^2}\left[W_k+V(r,\vartheta)\mp\hbar\left(\nu-\frac{eH}{2\mu c}-\frac{m\hbar}{\mu\sin^2\vartheta}\right)\right]\omega_H^{\pm}=\frac{\mu eEr\cos\vartheta}{\hbar^2}U_H(r,\vartheta). \quad (6)$$

The solution of Eq. (6) can be expressed in the form of the following double series:

$$\omega_H^{\pm}=\left[i\sum_m{}'e\hbar\Psi_m^{\pm}\cdot\int r\cos\vartheta u_{mk}(r,\vartheta)\Psi_m^{\pm}\,dv\cdot\int^t\exp i\left[(W_k-W_m\pm\hbar\nu)(t-\tau)\pm\frac{e\hbar}{2\mu c}\int_\tau^t H\,d\tau\right]d\tau\right\}\times E=\sum_m{}'\Psi_m^{\pm}\sum_n{}'\frac{(\pm1)^n n!\,f_{nm}^{\pm}(t)}{[W_k-W_m\pm\hbar(\nu-\nu_L)]^{n+1}}. \quad (7)$$

Here W_m and $\Psi_m^{\pm}$ are the eigenvalues and eigenfunctions of Eq. (6) without the right hand member when H and ν equal zero, and $f_{nm}^{\pm}(t)$ are time-dependent functions defined by the following differential equations:

$$\frac{\partial f_{nm}^{\pm}}{\partial t}+\frac{i}{\hbar}[W_k-W_m\pm\hbar(\nu-\nu_L)]f_{nm}^{\pm}=\frac{\nu_L}{2}f_{(n-1)m}^{\pm};\qquad \nu_L=\frac{eH}{2\mu c}. \quad (8)$$

Consequently,

$$f_{nm}^{\pm}=\int^t\exp i\left[(W_k-W_m\pm\hbar\nu)(t'-\tau)\mp\hbar\int_\tau^t\nu_L d\tau\right]\cdot\frac{\nu_L}{2}f_{m(n-1)}^{\pm}\,d\tau, \quad (9)$$

where the f_{nm} are constants selected in such a way that for H = 0 the quantity

$$\omega_0^{\pm}=\sum_m{}'f_{m0}^{\pm}\Psi_m^{\pm} \quad (10)$$

resents the solution of Eq. (6)

Breaking off the series in Eq. (7) at the n-th term, shall approximate the exact solution of Eq. (6) by ns of the remaining n terms with a relative error rder

$$\frac{(\dot{\nu}_L\hbar^2)^n}{[W_k - W_m \pm \hbar(\nu-\nu_L)]^{2n}}. \qquad (11)$$

Knowing $\omega_0^{\pm}$, we can find the complex index of re- tion of isolated molecules whose electrons have the e functions given by Eq. (3).[5]

When

$$\frac{\dot{\nu}_L\hbar^2}{[W_k - W_m \pm \hbar(\nu-\nu_L)]^2} \ll 1,$$

an take two terms in the summation over n in Eq. considering that

$$f_{1m} \approx \frac{f_{0m}\dot{\nu}_L\hbar}{i[W_k - W_m \pm \hbar(\nu-\nu_L)]}.$$

By straightforward calculation we therefore obtain the value of the complex refractive index,

$$n^2 - 1 = \frac{2Ne^2}{3h}\sum{}'\frac{\nu_{mk}|x_{mk}|^2}{\nu_{mk}^2-(\nu-\nu_L)^2} \times\left\{1 + i\frac{2\dot{\nu}_L(\nu-\nu_L)[3\nu_{mk}^2-(\nu-\nu_L)^2]}{\nu_{mk}[\nu_{mk}^2-(\nu-\nu_L)^2]^2}\right\}. \qquad (12)$$

re

$$\nu_{mk} = \frac{W_k - W_m}{\hbar}; \quad x_{mk} = \int r\cos\vartheta u_H(r,\vartheta)\Psi_m dv.$$

Equation (12) shows that if in the absence of a mag- c field the refractive index for a right-circular wave n optical medium is given by the expression

$$n_0^2 - 1 = \sum\frac{a_n}{\nu_n^2-\nu^2},$$

a longitudinal magnetic field is then applied, the re- tive index in the presence of the field can be found m the formula:

$$n_H^2 - 1 = \sum\frac{a_n}{\nu_n^2-(\nu-\nu_L)^2} \times\left\{1 + i\frac{2\dot{\nu}_L(\nu-\nu_L)[3\nu_n^2+(\nu-\nu_L)^2]}{\nu_n[\nu_n^2-(\nu-\nu_L)^2]^2}\right\}. \qquad (13)$$

The analogous formula for left-circular waves dif- s from Eq. (13) only in that it is necessary to write and $-\dot{\nu}_L$ for ν_L and $\dot{\nu}_L$.

Formulas (12) and (13) are invalid in the anomalous orption region, however, since a method based on the of perturbation theory is inapplicable in this case, it is necessary to look for another approximation to exact solution of Eq. (1). We shall seek an approxi- e solution to Eq. (1) in the form

$$\Psi \approx a_0(t)U_k + \sum a_n(t)\Psi_n, \qquad (14)$$

ere $a_n(t)$ is a coefficient that depends solely on time Ψ_n is one of the eigenfunctions of Eq. (2) whose en- y differs from the ground state energy by

$$\hbar\nu \approx W_k - W_n \qquad (15)$$

the matrix elements of whose transitions to the und state differ from zero. By applying a constant magnetic field which resolves the degeneracy of the Ψ_n function (in addition to the alternating field), we can in- sure that only one of these functions fulfills the condi- tion of Eq. (15). This allows us to use a two-term approxi- mation, which greatly simplifies all calculations. We shall seek an approximate solution in the form

$$\Psi \approx a_0(t)U_k + a_1(t)\Psi_n, \qquad (16)$$

where

$$\Psi_n = \Psi(r,\vartheta)\exp\left[i(m+1)\varphi - i\frac{W_n}{\hbar}t + \frac{e(m+1)}{2\mu c}i\int^t Hd\tau\right]. \qquad (17)$$

Substituting Ψ into Eq. (1), we obtain

$$\frac{2i\mu}{\hbar}U_H\frac{\partial a_0}{\partial t} + \frac{2i\mu}{\hbar}\Psi_n\frac{\partial a_1}{\partial t} - \frac{\mu Eer\cos\vartheta}{\hbar^2}[\exp i(\nu t+\varphi) + \exp i(-\nu t-\varphi)] \times(a_0U_H + a_1\Psi_n) = 0. \qquad (18)$$

Multiplying Eq. (18) by Ψ_n^* and U_H^*, and integrating the right and left sides of the two new equations over all space, we obtain

$$\left.\begin{aligned}\frac{2i\mu}{\hbar}\frac{\partial a_1}{\partial t} &= \frac{\mu eE}{\hbar^2}a_0\exp\left(i\nu t - i\frac{W_k-W_n}{\hbar} - \frac{ei}{2\mu c}\int^t Hd\tau\right)\int u_k r\psi_n^*\cos\vartheta dv,\\ \frac{2i\mu}{\hbar}\frac{\partial a_0}{\partial t} &= \frac{\mu eE}{\hbar^2}a_1\exp\left(-i\nu t + i\frac{W_k-W_n}{\hbar} + \frac{ei}{2\mu c}\int^t Hd\tau\right)\int u_k^* r\psi_n\cos\vartheta dv.\end{aligned}\right\} \qquad (19)$$

Symbolizing $\nu t - [(W_k - W_n)/\hbar] - (ei/2\mu c)\int_t Hd\tau$ by ε, and $(eE/2\hbar i)\int\psi_n^* r\cos\theta u_H dv$ by F_{kn}, Eq. (19) is trans- formed to

$$\left.\begin{aligned}\dot{a}_0 &= -F_{kn}^*\exp(-i\varepsilon)\cdot a_1,\\ \dot{a}_1 &= F_{kn}\exp i\varepsilon\cdot a_0.\end{aligned}\right\} \qquad (20)$$

It is easy to verify that this system is equivalent to the following:

$$\left.\begin{aligned}\ddot{a}_0 - i\dot{\varepsilon}\dot{a}_0 + |F_{kn}|^2 a_0 &= 0,\\ \ddot{a}_1 + i\dot{\varepsilon}\dot{a}_1 + |F_{kn}|^2 a_1 &= 0.\end{aligned}\right\} \qquad (21)$$

If in place of a_0 and a_1 we substitute $b_0\exp(i\varepsilon/2)$ and $b_1\exp(-i\varepsilon/2)$, respectively, we obtain the following two equations in b_0 and b_1:

$$\left.\begin{aligned}\ddot{b}_0 + \left(|F_{kn}|^2 - i\frac{\ddot{\varepsilon}}{2} + \frac{\dot{\varepsilon}^2}{4}\right)b_0 &= 0,\\ \ddot{b}_1 + \left(|F_{kn}|^2 + i\frac{\ddot{\varepsilon}}{2} + \frac{\dot{\varepsilon}^2}{4}\right)b_1 &= 0.\end{aligned}\right\} \qquad (22)$$

We shall consider the solution of Eqs. (22) for H = const; the terms containing H can be neglected because of their smallness. Apparently this takes place in a time interval $\Delta t \ll 1/\dot{\varepsilon}$ after the application of the alter- nating magnetic field. In this case the integration of Eqs. (22) is elementary. This permits the determination of Ψ satisfying the initial conditions[6]

$$a_0(0) = 1, \quad a_1(0) = 0,$$

$$\Psi = \Psi_k\left\{\exp\frac{i\varepsilon}{2}\cdot\cos\sqrt{\frac{\dot{\varepsilon}^2}{4}+|F_{kn}|^2 - \frac{i\ddot{\varepsilon}}{2}}\,t - \frac{i\dot{\varepsilon}\exp\frac{i\varepsilon}{2}}{2\sqrt{\frac{\dot{\varepsilon}^2}{4}+|F_{kn}|^2-\frac{i\ddot{\varepsilon}}{2}}}\right. \qquad (23)$$

$$\left.\sin\sqrt{\frac{\dot{\varepsilon}^2}{4}+|F_{kn}|^2-\frac{i\ddot{\varepsilon}}{2}}\,t\right\} - \Psi_n\frac{F_{nk}^*\exp\frac{-i\varepsilon}{2}}{\sqrt{\frac{\dot{\varepsilon}^2}{4}+|F_{kn}|^2+\frac{i\ddot{\varepsilon}}{2}}}$$

$$\times\sin\sqrt{\frac{\dot{\varepsilon}^2}{4}+|F_{kn}|^2+\frac{i\ddot{\varepsilon}}{2}}\,t. \qquad (24)$$

Assuming that F_{nn} and F_{kk} are zero, we obtain for the complex refractive index[5]:

$$n_H^2 - 1 = \frac{Ne^2 |r_{nk}|^2}{3h} \left\{ \frac{\nu - \nu_{kn} - \nu_L}{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 - 2i\dot{\nu}_L} \right.$$

$$+ \frac{i \sin \sqrt{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 + 2i\dot{\nu}_L}}{\sqrt{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 + 2i\dot{\nu}_L}} - \quad (25)$$

$$\left. - \frac{(\nu - \nu_{kn} - \nu_L) \cos \sqrt{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 + 2i\dot{\nu}_L}\, t}{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 + 2i\dot{\nu}_L} \right\}.$$

The mean value of the refractive index for systems for which the real lifetime of the excited state equals $1/\gamma$ can be estimated from the formula

$$\overline{n_H^2 - 1} = \gamma \int_0^\infty (n_H^2 - 1) \exp(-\gamma t)\, dt. \quad (26)$$

Integration yields

$$\overline{n_H^2 - 1} = \frac{Ne^2 |r_{nk}|^2}{3h} \frac{\nu - \nu_{kn} - \nu_L + i\gamma}{(\nu - \nu_{kn} - \nu_L)^2 + 4|F_{kn}|^2 + \gamma^2 - 2i\dot{\nu}_L} \quad (27)$$

It should be noted that Eq. (27) is valid for the case

$$|\gamma| \gg |\nu - \nu_{kn} - \nu_L|,$$

for which

$$\overline{n_H^2 - 1} \approx \frac{Ne^2 |x_{nm}|^2}{3h} \frac{i\gamma}{4|F_{kn}|^2 + \gamma^2 - 2i\dot{\nu}_L}. \quad (28)$$

In the optical region, as a rule,

$$|F_{kn}|^2 \ll \gamma^2.$$

Hence,

$$\overline{n_H^2 - 1} \approx \frac{Ne^2 |x_{nm}|^2}{3h} \frac{i\gamma}{\gamma^2 - 2i\dot{\nu}_L} = \overline{(n_0^2 - 1)} \frac{1}{1 - \frac{2i\dot{\nu}_L}{\gamma^2}}. \quad (29)$$

Here $\bar{n}_0$ is the refractive index for a right-circular wave in the absence of an alternating magnetic field.

An analogous formula for left-circular polarization can be obtained by replacing $\dot{\nu}_L$ by $-\dot{\nu}_L$. Equations (13) and (29) are correct for a system of molecules with several electrons whose spins are compensated, and the projection of the total orbital moment of the electrons on a given direction in space (in our case this is the direction of the magnetic field intensity vector) is equal to zero or an integral multiple of $\hbar$.[6] *

*Actually, the formulas derived will be valid only in the case $(1/n)(\partial n/\partial t) \cdot (1/\nu) \ll 1$, i.e., when the relative change in the index over one cycle is much smaller than unity.[1]

As examples of such systems one can cite pairs of elements containing an even number of electrons, such as the majority of the diatomic and inert gases.

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A MOLECULAR THEORY OF REFRACTION OF LIGHT IN CRYSTALS

B. A. Sotskii (pp. 229-236)

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A molecular theory of the reflection and refraction of light by transparent crystals contiguous to a vacuum or an isotropic medium is proposed. A strict molecular basis is presented for the condition of total polarization, and the physical meaning of Brewster's law is defined more accurately.

In the classic papers by Ewald[1] a molecular basis is given for the laws of propagation, refraction, and reflection of plane electromagnetic waves in crystals; and expressions for the dispersion and an equation of the normals were obtained for a crystal of any form. However Ewald derived amplitude ratios only for a cubic crystal which is isotropic in optical behavior. Until now Fresnel formulas have not been derived from molecular theory for anisotropic crystals apparently because of the extreme complexity of their form for the general case of a crystal, and also due to specific difficulties associated with the presence of two waves in the crystals.

Recently[2] the formulas under consideration for the amplitudes of the reflected and refracted waves in transparent crystals have been derived in vector form by phenomenological means on the basis of an invariant method.

The object of this work is to present a rigorous molecular basis for Fresnel's formulas for a transparent crystal of any type contiguous to a vacuum or an isotropic medium.

Let a plane electromagnetic wave* fall from a vacuum onto the plane boundary of a crystalline medium (see Fig. 1).

$$\mathbf{E} = \mathbf{E}_0 e^{i(\omega t - \mathbf{m}\mathbf{r})} \quad (m^2 = 1). \tag{1}$$

Under the influence of this wave some state of oscillation of dipoles develops in the crystal. As usual we assume that the state can be described by a plane dipole wave

$$\mathbf{p}_l = \mathbf{p} e^{i(\omega t - \mathbf{m}''\mathbf{r}_l)}. \tag{2}$$

Here $\mathbf{p}_l$ is the electric moment of the l-th dipole, $\mathbf{p}$ is the amplitude of the dipole oscillation, $\mathbf{m}''$ is the vector of refraction of the dipole wave, $\mathbf{r}_l = l_i \mathbf{a}_i$ (i = 1, 2, 3), where the $\mathbf{a}_i$ are base vectors of the crystal lattice, and the l_i are any integers, including zero. There exists a general connection between the dipole moment and the effective electric field $\mathbf{E}_{\text{eff}}$.

$$\frac{1}{V} \alpha^{-1} \mathbf{p} = \mathbf{E}_{\text{eff}}, \tag{3}$$

where α is the tensor polarizability of the molecule-dipole, relative to the size of the elementary cell (we assume for simplicity one dipole per elementary cell), and V is the volume of an elementary cell. The effective field at the point $\mathbf{r}_1 = 0$ is determined by the following series[1]:

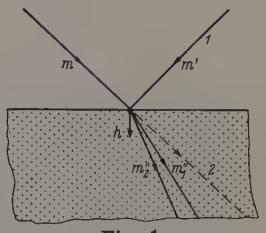

Fig. 1

$$\mathbf{E}_{\text{eff}} = \lim_{r \to 0} \sum_l{}' \operatorname{rot}\operatorname{rot} \frac{\mathbf{p} e^{i(\omega t - \mathbf{m}''\mathbf{r}_l - R)}}{R}, \tag{4}$$

where $R = \sqrt{\mathbf{r} - \mathbf{r}_l}$ and the primes indicate that the sum does not include the term $l_1 = l_2 = l_3 = 0$. An effective method of calculating similar "lattice" sums using a Fourier-transformation of the θ function was pointed out by Ewald (see ref. 1 and also 3). Moreover, in this method the indicated summation can be represented as the sum of two terms, one of which gives the average field and the second the "internal" field which is rapidly alternating from atom to atom,

$$\mathbf{E}_{\text{eff}} = \mathbf{E}'' + 4\pi\beta\mathbf{P}''. \tag{5}$$

Here $\mathbf{E}''$ is the average (Maxwellian) field, $\mathbf{P}'' = \mathbf{p}/V$ is the polarization vector, and β is a known tensor[4] depending on the structure of the crystal lattice. We will not write down the expression for the tensor here. For the case of optical waves ($|\mathbf{a}_i| \ll 1$) the tensor β can be considered as independent of $\mathbf{m}''$ in the zero approximation. In this same approximation, according to refs. 1 and 3, the average field is connected with the polarization vector in the following way*:

$$\mathbf{E}'' = \frac{4\pi}{n''^2 - 1} (1 - \mathbf{m}'' \cdot \mathbf{m}'') \mathbf{P}''. \tag{6}$$

Equation (3) may be written in the following form when expressions (5) and (6) are taken into account

$$\alpha^{-1}\mathbf{P}'' = \frac{4\pi}{n''^2 - 1} (1 - \mathbf{m}'' \cdot \mathbf{m}'') \mathbf{P}'' + 4\pi\beta\mathbf{P}''. \tag{7}$$

The tensors α^{-1} and β entering into this equation can be expressed in terms of the tensor dielectric permeability ε. On taking into account expressions (3) and (5) and also the definition of the vector $\mathbf{D}$ we obtain

$$\alpha^{-1} - 4\pi\beta = 4\pi (\varepsilon - 1)^{-1}. \tag{8}$$

The condition (7) may now be rewritten in the following way:

*Values having the dimension of length are assumed to be measured in units of $\lambda/2\pi$, where λ is the wavelength in the light in the vacuum, the vector $\mathbf{m} = n\mathbf{n}$, where n is the index of refraction, and $\mathbf{n}$ is the unit vector of the wave normal.

*If two vectors stand side by side in the formula their scalar product is indicated; a dot placed between the two vectors indicates that the components of these vectors enter independently (dyad).

$$\left\{\frac{4\pi}{n''^2-1}(1-\mathbf{m}''\cdot\mathbf{m}'')-4\pi(\varepsilon-1)^{-1}\right\}\mathbf{P}''=0. \quad (9)$$

According to (6),

$$\mathbf{P}''=\frac{1}{4\pi}(n''^2-1-\mathbf{m}''\cdot\mathbf{m}'')\mathbf{E}''. \quad (10)$$

Substitution of (10) in (9) yields after several transformations

$$(n''^2-\varepsilon-\mathbf{m}''\cdot\mathbf{m}'')\mathbf{E}''=0. \quad (11)$$

Setting the determinant of this equation equal to zero we obtain the equation of the normals in invariant form[2]

$$|n''^2-\varepsilon-\mathbf{m}''\cdot\mathbf{m}''|=0. \quad (12)$$

As is known, it follows from here that there are two values for the index of refraction, one corresponding to each direction of propagation. Consequently it can be expected in our case that in general there will appear in the crystal two dipole waves, the vectors of refraction of which must satisfy the equation of the normals. Moreover, these waves are propagated in different directions. One of the equations of the normals is not sufficient to determine the vectors of refraction.

Let us assume in conformity with what has been said that there are two dipole waves in the crystal:

$$\mathbf{P}_1''=\mathbf{P}_{10}''e^{i(\omega t-\mathbf{m}_1''\mathbf{r})};\quad \mathbf{P}_2''=\mathbf{P}_{20}''e^{i(\omega t-\mathbf{m}_2''\mathbf{r})}, \quad (13)$$

moreover $\mathbf{m}_1''$ and $\mathbf{m}_2''$ satisfy Eq. (12). Each of these dipole waves produces its vacuum wave both inside the crystal and outside (see ref. 5). We designate these respectively $\mathbf{E}_{12}$, $\mathbf{E}_{11}$, $\mathbf{E}_{22}$, $\mathbf{E}_{21}$, where the first index indicates from which dipole wave the given vacuum wave originates and the second index shows the direction of its propagation. The expressions for $\mathbf{E}_{1k}$ obtained in ref. 1 can be written in the following form

$$\left.\begin{aligned}&\mathbf{E}_{12}=4\pi\varphi_1e^{-i\mathbf{m}_1\mathbf{r}}[\mathbf{m}_2[\mathbf{m}_2\mathbf{P}_{10}'']],\ \mathbf{E}_{11}=4\pi\varphi_1'e^{-i\mathbf{m}_1'\mathbf{r}}[\mathbf{m}_1[\mathbf{m}_1\mathbf{P}_{10}'']],\\&\mathbf{E}_{22}=4\pi\varphi_2e^{-i\mathbf{m}_2'\mathbf{r}}[\mathbf{m}_2'[\mathbf{m}_2'\mathbf{P}_{20}'']],\ \mathbf{E}_{21}=4\pi\varphi_2'e^{-i\mathbf{m}_1'\mathbf{r}}[\mathbf{m}_1'[\mathbf{m}_1'\mathbf{P}_{20}'']].\end{aligned}\right\} \quad (14)$$

Here

$$\varphi_1=\frac{1}{2\mathbf{m}_2\mathbf{h}\cdot(\mathbf{m}_1''\mathbf{h}-\mathbf{m}_2\mathbf{h})},\quad \varphi_1'=\frac{1}{2\mathbf{m}_2\mathbf{h}\cdot(\mathbf{m}_1''\mathbf{h}+\mathbf{m}_2\mathbf{h})},$$

and φ_2 and φ_2' are obtained from φ_1 and φ_1' respectively by replacing $\mathbf{m}_1''$ by $\mathbf{m}_2''$; the vector $\mathbf{m}_2$ has the components

$$m_{1x}'',\ m_{1y}'',\ \sqrt{1-m_{1x}''^2-m_{1y}''^2},$$

and the vector $\mathbf{m}_1$ is symmetrical to the vector $\mathbf{m}_2$ relative to the interface plane. The vectors $\mathbf{m}_2'$

$$\left(m_{2x}'',\ m_{2y}'',\ \sqrt{1-m_{2x}''^2-m_{2y}''^2}\right)$$

and $\mathbf{m}_1'$ are also in the same proportion to each other ($\mathbf{h}$ is a unit vector along the normal to the surface of separation, see Fig. 1). The vacuum waves $\mathbf{E}_{12}$ and $\mathbf{E}_{22}$ propagating inside the crystal must damp the incident wave according to the theorem of Oseen. The vacuum waves outside the crystal, $\mathbf{E}_{11}$ and $\mathbf{E}_{21}$, superimposing, must give the reflected wave. Thus inside the crystal the correct equation is

$$\mathbf{E}_0e^{-i\mathbf{mr}}+4\pi\varphi_1[\mathbf{m}_2[\mathbf{m}_2\mathbf{P}_{10}'']]e^{-i\mathbf{m}_2\mathbf{r}}+4\pi\varphi_2[\mathbf{m}_2'[\mathbf{m}_2'\mathbf{P}_{20}'']]e^{-i\mathbf{m}_2'\mathbf{r}}=0, \quad (15)$$

which expresses Oseen's extinction theorem for crystals. The necessary condition of fulfillment of Eq. (15) is the relationship

$$\mathbf{m}=\mathbf{m}_2=\mathbf{m}_2'. \quad (16)$$

This condition is equivalent to the geometrical law of refraction. Using (16) and the symmetry of the vectors $\mathbf{m}_1$ and $\mathbf{m}_2$ as well as $\mathbf{m}_1'$ and $\mathbf{m}_2'$, we obtain the geometrical law of reflection

$$\mathbf{m}_1=\mathbf{m}_1'=\mathbf{m}', \quad (17)$$

where $\mathbf{m}'$ is the vector of refraction of the reflected wave. Now the relationship (15) takes the form

$$\mathbf{E}_0+4\pi\varphi_1[\mathbf{m}[\mathbf{m}\mathbf{P}_{10}'']]+4\pi\varphi_2[\mathbf{m}[\mathbf{m}\mathbf{P}_{20}'']]=0. \quad (18)$$

The geometrical law of refraction makes it possible to determine only those components of the vectors of refraction of the refracted waves which lie in the division plane. The normal components $\mathbf{m}_1''$ and $\mathbf{m}_2''$ are found from the equation of the normals.

Using the extinction theorem (18) and Eq. (11) we find the amplitude of the refracted rays. Expressing $\mathbf{P}_{10}''$ and $\mathbf{P}_{20}''$ (18) in terms of $\mathbf{E}_1''$ and $\mathbf{E}_2''$, then multiplying (18) vectorially by $\mathbf{m}$, we obtain

$$[\mathbf{m}\mathbf{E}_0]-\varphi_1[\mathbf{m},(\varepsilon-1)\mathbf{E}_1'']-\varphi_2[\mathbf{m},(\varepsilon-1)\mathbf{E}_2'']=0. \quad (19)$$

It follows from Eq. (11) that

$$\mathbf{E}_1''=A_1(\varepsilon-n_1''^2)^{-1}\mathbf{m}_1'',\quad \mathbf{E}_2''=A_2(\varepsilon-n_2''^2)^{-1}\mathbf{m}_2''. \quad (20)$$

The scalar amplitudes A_1 and A_2 are found from (19). Substituting (20) in (19) and scalarly multiplying the resultant equation by $\mathbf{h}$ and by $[\mathbf{mh}]$, we obtain A_1 and A_2:

$$A_1=\frac{1}{\varphi_1}\cdot\frac{L_{42}^{(2)}\mathbf{E}_0\mathbf{h}-\mathbf{E}_0[\mathbf{mh}]\left\{L_{32}^{(2)}-\mathbf{mh}\cdot\mathbf{m}L^{(2)}\mathbf{m}_2''\right\}}{L_{42}^{(2)}L_{31}^{(1)}-L_{41}^{(1)}L_{32}^{(2)}+L_{41}^{(1)}\mathbf{mh}\cdot\mathbf{m}L^{(2)}\mathbf{m}_2''-L_{42}^{(2)}\mathbf{mh}\cdot\mathbf{m}L^{(1)}\mathbf{m}_1''}, \quad (21)$$

where

$$L^{(i)}=(\varepsilon-1)(\varepsilon-n_i''^2)^{-1}\ (i=1,2),\ L_{ki}^{(i)}$$

are numbers obtained by scalar multiplication of the tensor $L^{(i)}$ from the left and from the right by the vectors $\mathbf{m}_1'$, $\mathbf{m}_2'$, $\mathbf{h}$, $[\mathbf{mh}]$, to which are respectively attached the indices 1, 2, 3, 4 (for example

$$L_{32}^{(2)}=\mathbf{h}L^{(2)}\mathbf{m}_2'');$$

A_2 is obtained from A_1 by transposition of the indices $1 \rightleftarrows 2$.

Formula (21) gives the amplitude of the refracted wave for any orientation of the crystal with the exception of the case of normal incidence. We will look at this case separately. Since in addition $\mathbf{m}\parallel\mathbf{m}_1''\parallel\mathbf{m}_2''\parallel\mathbf{h}$, in place of (19) we then have, according to (10),

$$[\mathbf{m}\mathbf{E}_0]+A_1\varphi_1(n_1''^2-1)[\mathbf{m}\mathbf{l}_1]+A_2\varphi_2(n_2''^2-1)[\mathbf{m}\mathbf{l}_2]=0, \quad (22)$$

where

$$\mathbf{l}_1=(\varepsilon-n_1''^2)^{-1}\mathbf{m}_1'',\ \mathbf{l}_2=(\varepsilon-n_2''^2)^{-1}\mathbf{m}_2''.$$

Let us multiply (22) scalarly by two linearly independent vectors $\mathbf{c}$ and $\mathbf{c}_1=[\mathbf{mc}]$ ($\mathbf{c}$ is any vector). Solving the system for A_1 and A_2 we obtain

$$A_1=\frac{\mathbf{E}_0\mathbf{c}_1\cdot\mathbf{c}_2\mathbf{l}_2-\mathbf{E}_0\mathbf{c}_2\cdot\mathbf{c}_1\mathbf{l}_2}{\varphi_1(n_1''^2-1)(\mathbf{c}_1\mathbf{l}_1\cdot\mathbf{c}_2\mathbf{l}_2-\mathbf{c}_2\mathbf{l}_1\cdot\mathbf{c}_1\mathbf{l}_2)}, \quad (2$$

where $\mathbf{c}_2=[\mathbf{m}[\mathbf{mc}]]$ (A_2 is obtained from A_1 by means of the above indicated substitutions). After simple calculations in the case of a uniaxial crystal, taking as the vector $\mathbf{c}$ a unit vector of the optic axis, we obtain a result fully in agreement with phenomenological formulas.[2] It

not hard to satisfy oneself that such agreement occurs all the remaining particular cases considered in ref. 2.

Let us now examine the problem of the principal ectors of the oscillations of the incident and reflected aves (see ref. 2). In other words let us find a state of larization of the incident wave such that it will be associated with only one refracted wave in the crystal. If assume that in the extinction theorem (19) $\mathbf{P}''_{20} = 0$ en the first principal vector of the incident wave will determined:

$$[\mathbf{mE}_0] - \varphi_1 (n_1''^2 - 1)[\mathbf{mE}_1''] + \varphi_1 \mathbf{m}_1'' \mathbf{E}_1'' \cdot [\mathbf{mm}_1''] = 0. \qquad (24)$$

sing the multiple vector product in expression (29.5) of f. 2 and taking into account the parallelism of the vectors [mh] and [mm$_1''$] we obtain Eq. (24) exactly. Agreement of the equations for determining the second principal vectors derived by the molecular and phenomenological methods can be established similarly by assuming $\mathbf{P}''_{10} = 0$ in (19).

Let us consider the reflected wave. The latter will be equal to the sum of the vacuum waves produced by the refracted waves in the external part of the volume, at is,

$$\mathbf{E}' = \mathbf{E}_{11} + \mathbf{E}_{21} \qquad (25)$$

substituting $\mathbf{E}_{11}$ and $\mathbf{E}_{21}$ from (14),

$$\mathbf{E}' = -4\pi [\mathbf{m}' [\mathbf{m}', \varphi_1' \mathbf{P}''_{10} + \varphi_2' \mathbf{P}''_{20}]] e^{-i\mathbf{m}'\mathbf{r}}. \qquad (26)$$

Assuming in (26) $\mathbf{P}''_{20} = 0$, multiplying vectorially by m$'$ and replacing $\mathbf{P}''_{10}$ according to (10), we have for the principal direction of polarization in the reflected wave

$$[\mathbf{m}'\mathbf{E}'] = \mathbf{H}' = \varphi_1' \mathbf{m}_1 \mathbf{E}_1'' \cdot [\mathbf{m}'\mathbf{m}_1] - \varphi_1' (n_1''^2 - 1)[\mathbf{m}'\mathbf{E}_1'']. \qquad (27)$$

Here H$'$ is the magnetic field of the reflected wave. is not difficult to convince oneself that in this case the olecular theory gives the same result as the phenomeological.[2]

Thus the above shows, in the same general form, the greement of the amplitude ratios derived by molecular nd phenomenological methods for the case of a light wave cident on a crystal from a vacuum.

Formula (26) makes it possible to obtain easily the ondition of total polarization of the reflected wave. Multiplying (26) vectorially by m$'$, we get, dropping the calar multiplier,

$$\mathbf{H}' = -[\mathbf{m}', \varphi_1' \mathbf{P}''_{10} + \varphi_2' \mathbf{P}''_{20}]. \qquad (28)$$

After vector multiplication of expression (28) by the omplex conjugate equation and taking into account the act that as a consequence of the linear polarization of ne refracted waves[2]

$$P''_{10} = a_1 \Pi_1, \quad P''_{20} = a_2 \Pi_2,$$

here a_1 and a_2 are some complex numbers and Π_1 and Π_2 are real vectors, we obtain

$$[\mathbf{H}'\mathbf{H}'^*] = (a_1 a_2^* - a_2 a_1^*)\, \mathbf{m}' [\Pi_1 \Pi_2] \cdot \mathbf{m}'. \qquad (29)$$

The reflected wave will be linearly polarized under ne condition that $a_1 a_2^* - a_2 a_1^* = 0$ or

$$\mathbf{m}' [\Pi_1 \Pi_2] = 0. \qquad (30)$$

The first case is trivial (a linearly polarized wave s-incident on the crystal). Equation (30) itself, giving ne molecular condition of total polarization of the reected wave in the general case, agrees exactly with the ondition which was obtained in ref. 2.

Let us now look at the case of reflection and refrac-

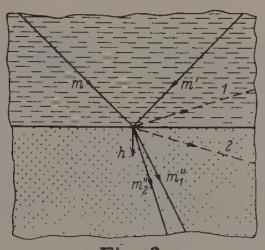

Fig. 2

tion of light at the boundary of an isotropic medium and a crystal. Let the isotropic medium occupy the upper half-volume and the crystal the lower (Fig. 2).

Along the direction m in the isotropic medium is propagated a dipole wave (incident)

$$\mathbf{P} = \mathbf{P}_0 e^{i(\omega t - \mathbf{mr})}, \qquad (31)$$

where m is the vector of refraction of the incident wave. In addition to wave (31) there will be a reflected dipole wave in the isotropic medium, and in the crystal there will be two refracted dipole waves. Each of these dipole waves (see ref. 5) produces two vacuum waves one of which is propagated along direction 1, the other along direction 2 (Fig. 2). The condition of dynamic equilibrium of all four dipole waves is the mutual extinction of all the vacuum waves propagating both along direction 1 and direction 2. The condition of extinction is written in the following way (see expression 14 and also ref. 5):

$$N_1 \mathbf{P}_0 + L_1 \mathbf{P}_0' + 4\pi\varphi_1' [\mathbf{m}_1 [m_1 \mathbf{P}''_{10}]] + 4\pi\varphi_2' [\mathbf{m}_1 [\mathbf{m}_1 \mathbf{P}''_{20}]] = 0 \qquad (32)$$

for the isotropic medium and

$$N_2 \mathbf{P}_0 + L_2 \mathbf{P}_0' + 4\pi\varphi_1 [\mathbf{m}_2 [\mathbf{m}_2 \mathbf{P}''_{10}]] + 4\pi\varphi_2 [\mathbf{m}_2 [\mathbf{m}_2 \mathbf{P}''_{20}]] = 0 \qquad (33)$$

for the crystal. Here $\mathbf{P}_0'$ is the amplitude of the reflected dipole wave, $\mathbf{m}_1$ and $\mathbf{m}_2$ are the vectors of refraction of the vacuum waves propagated respectively along directions 1 and 2 (Fig. 2). The expressions for N_i and L_i (i = 1, 2) are included in ref. 5. With their aid, multiplying Eq. (32) from the left by the operator L_1^{-1}, and (33) by L_2^{-1}, deducting the second result from the first, and taking into consideration that

$$\mathbf{E} = \frac{4\pi}{n^2 - 1} \mathbf{P}$$

(n is the index of refraction of the isotropic medium), we express the field of the incident wave in terms of the fields of the refracted waves:

$$\mathbf{E} = \frac{1}{4\mathbf{mh} \cdot \mathbf{m}_2\mathbf{h}} \left\{ \left[\frac{2\mathbf{m}_2\mathbf{h} \cdot (\mathbf{mh} + \mathbf{m}_1''\mathbf{h})}{n_1''^2 - 1} + \frac{\mathbf{mh} - \mathbf{m}_2\mathbf{h}}{\mathbf{m}_1''\mathbf{h} + \mathbf{m}_2\mathbf{h}} \cdot \frac{1}{\mathbf{mm}_2} \mathbf{m}_1 \cdot \mathbf{m}' \right.\right.$$
$$- \frac{\mathbf{mh} + \mathbf{m}_2\mathbf{h}}{\mathbf{m}_1''\mathbf{h} - \mathbf{m}_2\mathbf{h}} \cdot \frac{1}{\mathbf{mm}_1} \mathbf{m}_2 \cdot \mathbf{m}' - \frac{2\mathbf{m}_2\mathbf{h} \cdot (\mathbf{mh} + \mathbf{m}_1''\mathbf{h}) \cdot \mathbf{mm}_1 \cdot \mathbf{mm}_2}{n^2 (n_1''^2 - 1)} \mathbf{q} \cdot \mathbf{h}$$
$$\left.\left. + \frac{2\mathbf{m}_2\mathbf{h} \cdot (\mathbf{mh} \cdot \mathbf{m}_1''\mathbf{h} + (\mathbf{m}_2\mathbf{h})^2 n^2)}{n^2 (n_1''^2 - 1)} \mathbf{q} \cdot \mathbf{m}' \right] \mathbf{P}''_{10} + [\mathbf{m}_1'' \to \mathbf{m}_2''] \mathbf{P}''_{20} \right\}, \qquad (34)$$

where

$$\mathbf{q} = \frac{(\mathbf{mh} + \mathbf{m}_2\mathbf{h})^2}{2\mathbf{m}_2\mathbf{h} \cdot \mathbf{mm}_1} \mathbf{m}_2 - \frac{(\mathbf{mh} - \mathbf{m}_2\mathbf{h})^2}{2\mathbf{m}_2\mathbf{h} \cdot \mathbf{mm}_2} \mathbf{m}_1,$$

and the bracketed expression $[\mathbf{m}_1'' \to \mathbf{m}_2'']$ stands for the same expression as that in the first square brackets with replacement of $\mathbf{m}_1''$ by $\mathbf{m}_2''$. Then multiplying expression (32) from the left by N_1^{-1} and (33) by N_2^{-1} and subtracting the second result from the first we obtain the field of the

reflected wave:

$$E' = \frac{(\mathbf{m}_2\mathbf{h})^2 - (\mathbf{mh})^2}{4\mathbf{mh}\cdot\mathbf{m}_2\mathbf{h}}\left\{\left[\frac{2\mathbf{m}_2\mathbf{h}\cdot(\mathbf{m}_1''\mathbf{h}-\mathbf{mh})}{n_1''^2-1} + \frac{(\mathbf{mh}-\mathbf{m}_2\mathbf{h})(\mathbf{m}_1''\mathbf{h}+\mathbf{m}_2\mathbf{h}\cdot n^2)}{n^2(n_1''^2-1)}\mathbf{m}_2\cdot\mathbf{m} - \frac{(\mathbf{mh}+\mathbf{m}_2\mathbf{h})(\mathbf{m}_1''\mathbf{h}-\mathbf{m}_2\mathbf{h}\cdot n^2)}{n^2(n_1''^2-1)}\mathbf{m}_1\cdot\mathbf{m} - \frac{2\mathbf{m}_2\mathbf{h}\cdot(\mathbf{m}_1''\mathbf{h}-\mathbf{mh})\,\mathbf{mm}_1\cdot\mathbf{mm}_2}{n^2(n_1''^2-1)}\mathbf{q}'\cdot\mathbf{h}\right]\mathbf{P}_{10}'' + [\mathbf{m}_1'' \to \mathbf{m}_2'']\mathbf{P}_{20}''\right\}, \tag{35}$$

where

$$\mathbf{q}' = \frac{(\mathbf{mh}-\mathbf{m}_2\mathbf{h})^2}{2\mathbf{m}_2\mathbf{h}\cdot\mathbf{mm}_2}\mathbf{m}_2 - \frac{(\mathbf{mh}+\mathbf{m}_2\mathbf{h})^2}{2\mathbf{m}_2\mathbf{h}\cdot\mathbf{mm}_1}\mathbf{m}_1.$$

Let us find the principal vectors of the oscillations of the incident wave. Assuming that $\mathbf{P}_{20}'' = 0$ in Eq. (34) and multiplying it vectorially by $\mathbf{m}$, we obtain

$$2\mathbf{mh}\cdot[\mathbf{mE}] = (\mathbf{mh}+\mathbf{m}_1''\mathbf{n})[\mathbf{mE}_1''] - \frac{\mathbf{mh}+\mathbf{m}_1''\mathbf{h}}{n_1''^2-1}\mathbf{m}_1''\mathbf{E}_1\cdot[\mathbf{mm}_1''] + \frac{\mathbf{mh}+\mathbf{m}_2\mathbf{h}}{n_1''^2-1}[\mathbf{mm}_2]\cdot\mathbf{m}_1''\mathbf{E}_1''. \tag{36}$$

The relationship (10) is taken into account in writing expression (36). Since

$$[\mathbf{mm}_1''] = (\mathbf{m}_1''\mathbf{h}-\mathbf{mh})[\mathbf{mh}],$$

while

$$[\mathbf{mm}_2] = (\mathbf{m}_2\mathbf{h}-\mathbf{mh})\cdot[\mathbf{mh}],$$

(36) agrees with (24). Assuming $\mathbf{P}_{20}'' = 0$ or $\mathbf{P}_{10}'' = 0$ in (35), we find the principal directions of the reflected wave. For the first principal direction Eq. (27) is correct (after vectorially multiplying by $\mathbf{m}$ and conversion from $\mathbf{P}_6''$ to $\mathbf{E}_1''$). Thus in the most general case of refraction at the boundary of an isotropic medium and a crystal, the results of the molecular and phenomenological theories also fully agree.

Let us clarify what the conditions must be in the given case for total polarization of the reflected wave. From a calculation on the basis of (35) we have the law of refraction

$$2\mathbf{mh}\cdot[\mathbf{m}'\mathbf{E}'] = [\mathbf{m}', (\mathbf{mh}-\mathbf{m}_1''\mathbf{h})\cdot\mathbf{E}_1'' + \mathbf{h}\cdot\mathbf{m}_1''\mathbf{E}_1'' + (\mathbf{mh}-\mathbf{m}_2''\mathbf{h}) \times \mathbf{E}_2'' + \mathbf{h}\cdot\mathbf{m}_2''\mathbf{E}_2'']. \tag{37}$$

Supplementing from the right the second co-multiplier by the vector

$$\mathbf{m}'\cdot\left(\frac{\mathbf{m}_1''\mathbf{E}_1''}{\mathbf{m}_1''\mathbf{h}+\mathbf{mh}} + \frac{\mathbf{m}_2''\mathbf{E}_2''}{\mathbf{m}_2''\mathbf{h}+\mathbf{mh}}\right)$$

which does not change the vector product, we derive, according to (11),

$$-2\mathbf{mh}\cdot[\mathbf{m}'\mathbf{E}'] = \left[\mathbf{m}', \frac{1}{\mathbf{mh}+\mathbf{m}_1''\mathbf{h}}(\varepsilon-n^2)\mathbf{E}_1'' + \frac{1}{\mathbf{mh}+\mathbf{m}_2''\mathbf{h}}(\varepsilon-n^2)\mathbf{E}_2''\right]. \tag{38}$$

Analogous to the case of light incident from a vacuum (see above) we find that the reflected wave will be fully polarized if the vectors $\mathbf{m}'$, $(\varepsilon - n^2)\mathbf{E}_1''$, and $(\varepsilon - n^2)\mathbf{E}_2''$ lie in the same plane, that is,

$$\mathbf{m}'[(\varepsilon-n^2)\mathbf{E}_1'', (\varepsilon-n')\mathbf{E}_2''] = 0.$$

A similar condition was obtained in ref. 2 from initial assumptions that were not completely rigorous.

In conclusion we will consider the physical meaning of Brewster's law. In general it is restricted to the case of an isotropic medium adjacent to a vacuum (with the light incident from the vacuum), for which the situation is simply that the reflected wave is produced by radiation of the oscillating dipoles in the refracted wave; and since the angle between the directions of the reflected and refracted waves is equal to $\pi/2$, and the dipoles do not radiate along their axes, then the reflected wave is absent (if the vector $\mathbf{E}$ lies in the plane of incidence). The situation is more complicated when light from the medium is incident on the boundary of separation from the vacuum. Let a wave coming from the medium and with oscillations lying in the plane of incidence fall near Brewster's angle (Fig. 3). In this case, as before, the angle between the directions of propagation of the reflected and refracted waves is $\pi/2$. However, the usual simple explanation is obviously unsuitable since there are no dipoles in the second medium (vacuum). Also the direction of oscillation of the dipoles in the incident wave is not parallel to the direction of the reflected wave. The solution of the problem in the given case lies in the fact that the incident wave cannot produce vacuum wave 1, because direction 1 forms a right angle with the direction of the incident wave. Since vacuum wave 1 is absent there will also be no corresponding reflected wave. In the case of two isotropic media bordering on one another (see ref. 5 and also Fig. 2) the reflected wave will be absent when the sum of the vacuum waves produced by the incident and refracted waves and being propagated along direction 1 is equal to zero. For a crystal with light incident from a vacuum the reflected wave will be absent when the condition

$$\mathbf{m}' \parallel \varphi_1'\mathbf{P}_{10}'' + \varphi_2'\mathbf{P}_{20}'', \tag{39}$$

[see (26)] is fulfilled and when the light is incident on the crystal from an isotropic medium [see (38)] under the condition

$$\mathbf{m}' \parallel (\varepsilon - n^2)\left(\frac{1}{\mathbf{mh}+\mathbf{m}_1''\mathbf{h}}\mathbf{E}_1'' + \frac{1}{\mathbf{mh}+\mathbf{m}_2''\mathbf{h}}\mathbf{E}_2''\right). \tag{40}$$

As should be expected, condition (40) converts to (39) when n = 1. In the case of (40) there will be no vacuum waves produced by the incident and refracted waves being propagated along direction 1 (Fig. 2).

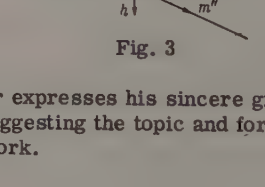

Fig. 3

The author expresses his sincere gratitude to F. I. Fedorov for suggesting the topic and for continued interest in the work.

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OPTICAL PRINCIPLE OF REVERSIBILITY AND ITS APPLICATION IN THE THEORY OF THIN-LAYER COATINGS

P. G. Kard (pp.237-241)

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The optical principle of reversibility is generalized to include the presence of absorbing media, and its application is demonstrated for the derivation of basic relationships in the theory of thin-layer coatings.

TRODUCTION

The present work was stimulated, on the one hand, the discovery of this writer[1] of a simplified form for e recurrence formulas by A. G. Vlasov, and on the her hand, by an article by Knittl,[2] in which the same rmulas are derived by a completely new method for the se when there is no absorption, namely, by the use of e reversibility principle. The principle of reversibility optics is usually considered inapplicable to the case of sorbing media. Therefore, at the end of his article, ittl expressed the opinion that the theory of the abrbing multilayer coatings can be based only on the Maxell boundary conditions. However, the principle of rersibility can be readily generalized to include the case absorbing media. Then this generalized reversibility inciple can be applied, by Knittl's method, to derive the currence formulas. This paper demonstrates that in is manner the same simplified Vlasov's formulas are tained which were derived by the writer by another ethod.[1]

Let us denote by n_0 and n the refractive indices of e initial medium and that of the substrate, by ϑ_0 the cidence angle, and by ϑ the angle of refraction in the bstrate. The refractive index and the thickness of an bitrarily selected intermediate layer inside of the ating shall be n_m and h_m, respectively, and the angle refraction in this layer shall be ϑ_m. We shall use the ime only for designation of quantities related to a ven coating in the case of incidence of light on it from e opposite direction, i.e., from the substrate side, at e incidence angle ϑ. As usual, a star will designate e complex conjugate quantities, and the sign ~ those antities which belong to the conjugate coating (see bew, and also ref. 1).

HE GENERALIZED REVERSIBILITY PRINCIPLE IN OPTICS

As mentioned before, in macroscopic electrodyamics the reversibility principle is usually applied only n the absence of conducting media. The principle states nat Maxwell's equations remain invariant under a time nversion ($t \to -t$) and a simultaneous transformation of ne charge density ($\rho \to \rho$) and the field vectors ($\mathbf{E} \to \mathbf{E}$, $\to \mathbf{D}$, and $\mathbf{H} \to -\mathbf{H}$, $\mathbf{B} \to -\mathbf{B}$). If there are conducting nedia, this does not apply because of the term $\sigma\mathbf{E}$ in the quations, where σ is the conductivity.

However, if we agree to transform the conductivity according to the rule $\sigma \to -\sigma$, then the equations again become invariant. In this manner we obtain the generalized reversibility principle which says: if an electrodynamic process of any kind is possible in a given medium, then in a medium which differs from the given one only by the sign of the conductivity, a process reversed with respect to time and differing from the given process only by the replacement of **H** and **B** by **−H** and **−B** is possible.

It is evident that the "possibility" of the reversed process is only of a formal nature, because there are no media with a negative conductivity. This means that electrodynamic processes in conducting media are actually irreversible. The principle of reversibility which is stated here does not abolish this elementary statement at all. From a purely logical point of view, we can imagine a medium with a negative conductivity and use this conception as an auxiliary one, for the derivation of the needed relationships.

In optics the transformation $\sigma \to -\sigma$ corresponds to a transition to the complex conjugate refractive indices of all media. In the theory of coatings this means the replacement of a given coating by a conjugate coating. By a coating conjugate with respect to a given one, we mean a coating in which the refractive indices (and, of course, also the angles of refraction, since Snell's refraction law remains the same) have complex conjugate values.

DERIVATION OF THE BASIC RELATIONSHIPS

We shall generalize the method of Knittl to include the case of any absorbing coating bounded by two semiinfinite media which we shall assume for the time being as nonabsorbing (Fig. 1). The incident, the reflected, and the transmitted rays shall be designated by the indices I, II, and III, respectively. The amplitude of the incident

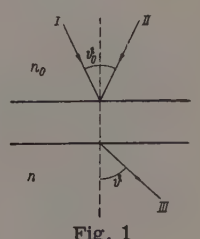

Fig. 1

ray we assume equal to unity, and the amplitudes of the rays II and III we shall denote by r and t. Now, if the rays II and III are reversed, then in the initial medium we obtain the reversed ray I, and in the substrate there will be no light, i.e.,

$$rr^* + tt'^* = 1, \tag{1}$$

$$rt^* + tr'^* = 0. \tag{2}$$

We find then

$$r' = -\frac{r^* t}{t^*} \tag{3}$$

and

$$t' = \frac{1 - rr^*}{t^*}, \tag{4}$$

as well as

$$rr^* = r'r'^*, \tag{5}$$

$$tt'^* = t't^*. \tag{6}$$

For the following, it is important to take into consideration that Eqs. (1) to (6) hold not only when the boundary media are transparent, but also when they are absorbing. This is due to the fact that the transparency condition of these media is not used except in the assumption that the "rays" I, II, III, which are actually plane waves, exist. However, if we write the expressions for the plane waves and use in them, instead of the real refractive indices and angles of incidence and refraction, the corresponding complex values, then for these expressions all the preceding considerations remain valid (inasmuch as we have used the generalized principle of reversibility). Consequently, Eqs. (1) to (6) will remain valid. It need only be remembered that in this case the amplitudes r and t have no simple connection with the energy coefficients of reflection and transmission. However, this is not essential for our purpose.

DERIVATION OF THE RECURRENCE FORMULAS

Next we arbitrarily select in the coating a layer (index m) which is either absorbing or nonabsorbing. It divides the coating into two subcoatings (Fig. 2), which will be denoted by the indices 1 (the one that is in the direction of the initial medium) and 2 (the one in the direction of the substrate). The incident and the reflected rays shall be denoted by I and II, the direct and the reversed rays in the intermediate layer by I_m and II_m, the transmitted ray by III. The amplitudes of the II and III rays shall be again r and t, and the amplitudes of the I_m and II_m rays shall be denoted by x and y, respectively. We also introduce the notation

$$kn_m h_m \cos\vartheta_m = \alpha, \tag{7}$$

where $k = 2\pi/\lambda$ is the wave number in vacuum.

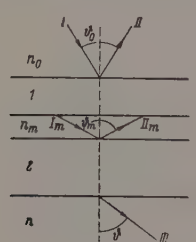

Fig. 2

Following Knittl again, we reverse the rays II, III, I_m, and II_m. Then we obtain the following equations (for details see the paper by Knittl, ref. 2)

$$rr_1^* + xt_1'^* = 1, \tag{8}$$

$$rt_1^* + xr_1'^* = e^{-i\alpha^*} y, \tag{9}$$

$$tt_2'^* + yr_2^* = e^{-i\alpha^*} x, \tag{10}$$

$$tr_2'^* + yt_2^* = 0. \tag{11}$$

The quantity $\tilde{\alpha}^*$ appearing in Eqs. (9) and (10) can immediately be replaced by α, because, according to (7), $\tilde{\alpha}^* = \alpha$. From Eqs. (10) and (11) we obtain

$$x = \frac{t}{t_2^*}\left(t_2^* t_2'^* - r_2^* r_2'^*\right) e^{i\alpha},$$

$$y = -\frac{tr_2'^*}{t_2^*}.$$

But, according to Eqs. (1) and (3),

$$t_2^* t_2'^* - r_2^* r_2'^* = \frac{t_2^*\left(t_2 t_2'^* + r_2 r_2'^*\right)}{t_2} = \frac{t_2^*}{t_2},$$

from which it follows that

$$x = \frac{te^{i\alpha}}{t_2}, \tag{12}$$

$$y = \frac{r_2 t}{t_2}. \tag{13}$$

By substituting these expressions into Eqs. (8) and (9) and calculating r and t (taking into consideration again Eqs. (1) and (3)), we obtain

$$r = \frac{r_1 + \frac{r_2 t_1}{t_1^*} e^{-2i\alpha}}{1 + \frac{r_2 r_1^* t_1}{t_1^*} e^{-2i\alpha}} \tag{14}$$

and

$$t = \frac{t_1 t_2 e^{-i\alpha}}{1 + \frac{r_2 r_1^* t_1}{t_1^*} e^{-2i\alpha}}. \tag{15}$$

These are the recurrence formulas being sought.

We shall make now some simple transformations.

The energy coefficient of reflection R (in those cases when it has an exact meaning, i.e., when the initial medium is transparent) is expressed in terms of the amplitude r by means of the formula

$$R = rr^*. \tag{16}$$

Therefore the quantity r is called the amplitude coefficient of reflection. The energy coefficient of transmission D (when it has an exact meaning, i.e., when both the initial medium and the substrate are transparent) is expressed in terms of t as

$$D = \frac{tt^* n\cos\vartheta}{n_0\cos\vartheta_0}. \tag{17}$$

Therefore, it is useful to introduce the quantity

$$d = t\sqrt{\frac{n\cos\vartheta}{n_0\cos\vartheta_0}} \tag{18}$$

(and similarly, d_1, d_2, d', etc.), so that

$$D = dd^*. \tag{19}$$

We shall call d (and not t) the amplitude coefficient of transmission (although t is often called by that name),

s shall extend the use of this term and of Eq. (18) to se cases in which the boundary media are absorbing, , in which Eq. (19) is not valid.

It is apparent from inspection of Eqs. (1)-(6), (14), (15) that they all retain their form after the substi- on $t \to d$. Indeed, since $\tilde{n}^* = n$ and $\tilde{\vartheta}^* = \vartheta$, then $= d/\tilde{d}^*$; in addition, $t\tilde{t}'^* = d\tilde{d}'^*$.

We shall now show how the known equality

$$d' = d. \tag{20}$$

ows from our equations.

To this end we shall write, in accordance with (15),

$$d' = \frac{d_1' d_2' e^{-i\alpha}}{1 + \frac{r_1' r_2'^* d_2'}{\tilde{d}_2'^*} e^{-2i\alpha}}.$$

Substituting in this expression r_1' and $\tilde{r}_2'^*$ according q. (3) (with d instead of t), and taking into account (6), we find

$$d' = \frac{d_1' d_2' e^{-i\alpha}}{1 + \frac{r_2 r_1^* d_1}{\tilde{d}_1^*} e^{-2i\alpha}}.$$

Consequently, the equality (20) holds, if it is valid the subcoatings. However, since this equality is al- s fulfilled for the Fresnel boundary between two dia, it is fulfilled for any coating.

Finally, we introduce the auxiliary quantities (see . 1)

$$\left.\begin{aligned} a &= \frac{r}{d}, \\ b &= \frac{1}{d}. \end{aligned}\right\} \tag{21}$$

Then Eqs. (1), (3), (14), (15), and (20) will have the m

$$\left.\begin{aligned} a' &= -\tilde{a}^*, \\ b' &= b, \end{aligned}\right\} \tag{22}$$

$$b\tilde{b}^* - a\tilde{a}^* = 1 \tag{23}$$

and

$$\left.\begin{aligned} a &= a_1 b_2 e^{i\alpha} + a_2 \tilde{b}_1^* e^{-i\alpha}, \\ b &= b_1 b_2 e^{i\alpha} + a_2 \tilde{a}_1^* e^{-i\alpha}. \end{aligned}\right\} \tag{24}$$

Those are the same expressions which we developed by another method in ref. 1.

CONCLUSION

We have shown how, by using the generalized principle of reversibility, one can obtain for optical coatings all the relationships which were formerly derived either by directly using the boundary conditions, or by Vlasov's method, i.e., by summation of the amplitudes of rays that underwent multiple reflections in the layers. The latter method, however, is not faultless (although it gives correct results), in the sense that the series are not always convergent (see refs. 3 and 4).

In comparison with the method that takes the boundary conditions into consideration explicitly, the method based on the principle of reversibility is simpler and may be considered more general, because in its application one does not have to assume that the coating consists of a finite number of homogeneous layers. Therefore, all results obtained by this method are valid also for coatings with a continuously changing refractive index. A similar conclusion is possible also by the use of other methods; however, it is then necessary to make a transition to the limit.

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THEORY OF LIGHT REFLECTION FROM A THIN ABSORBING FILM DEPOSITED ON A METAL

A. Vašíček* (pp. 242-247)
*The University, Brno, Czechoslovakia.

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From the general formula for light reflection by a thin layer, an expression is derived for the reflection of light by a thin metallic or semiconducting layer deposited on another metal. For the derivation of this formula, the Stokes principle of reversibility is used, along with the condition that for zero thickness of the thin metallic layer the reflection is the same as in the case of a pure metallic substrate without any surface layer. The formula is derived for the two simplest cases: for a layer of low absorption (semiconducting layer), in which case it is possible to consider a large number of reflections in a thin layer, and for a strongly absorbing metallic layer, in which case one may, for practical purposes, consider only one reflection of light from a thin metallic layer.

INTRODUCTION

The problem of the reflection of light by a thin absorbing layer located on another absorbing (metallic) layer concerns cases in which a thin metallic layer is placed upon another metallic substrate, or in which there is a contact with a semiconducting layer, as, for instance, Fe_2O_3 on steel, etc. Leberknight and Lustman[1] and later Winterbottom[2] studied problems of this kind, the latter author solving the problem graphically. The existing works on light reflection from a thin metallic layer located on another metallic layer are based on Maxwell's equations. However, according to Murmann,[3] they incorrectly generalize the boundary conditions for the complex amplitude of the reflected and refracted light at the first dielectric-metal boundary. The present writer, in his previous papers and especially in his book,[4] derived from Maxwell's theory general formulas for light reflection and transmission by a thin layer in the form:

$$r_R = \frac{r'_R + r''_R(t'_R t'_L - r'_R r'_L)e^{-i\varkappa}}{1 - r'_L r''_R e^{-i\varkappa}}, \tag{1}$$

$$t_R = \frac{t'_R t''_R e^{-i\frac{\varkappa}{2}}}{1 - r'_L r''_R e^{-i\varkappa}}. \tag{2}$$

In the derivation of these expressions, the direction of the light rays in the thin layer was taken into consideration. The complex amplitudes were denoted either by the index R for the motion of light to the right, or by the index L, for the motion to the left.

For brevity, we shall discuss only the case of the normal incidence of light ($\varphi_0 = 0°$), although this problem has been solved by the author for the general case of an arbitrary angle of incidence, and for both components of the polarized light, p and s.

If the index of refraction of the upper medium is denoted by n_0 (as a rule, this is air, with the index of refraction equal to unity) and the complex index of refraction of the thin metallic layer by $n_1 = n_1 - i\varkappa_1$, then the complex Fresnel amplitudes for light reflected from and transmitted through the first dielectric-metal boundary in the direction R (right), have the form:

$$r'_R = r'_R e^{i\vartheta'_R} = \frac{n_1 - n_0}{n_1 + n_0}, \tag{3}$$

$$t'_R = t'_R e^{i\vartheta'_R} = \frac{2n_0}{n_1 + n_0}, \tag{4}$$

where

$$r'^2_R = \frac{(n_1 - n_0)^2 + \varkappa_1^2}{(n_1 + n_0)^2 + \varkappa_1^2}, \tag{5}$$

$$t'^2_R = \frac{4n_0^2}{(n_1 + n_0)^2 + \varkappa_1^2}, \tag{6}$$

$$\tan\vartheta'_R = \frac{-2n_0\varkappa_1}{n_1^2 + \varkappa_1^2 - n_0^2}, \tag{7}$$

$$\tan\vartheta'_R = \frac{\varkappa_1}{n_1 + n_0}. \tag{8}$$

If the complex amplitudes r'_R and t'_R for the direction of light propagation to the right are given by Eqs. (3) and (4), then the complex amplitudes for the direction to the left (with the index L) are determined on the basis of the reversibility principle. In preceeding papers[5,6] the writer has shown that for the complex amplitudes r'_R, t'_R, r'_L, t'_L the principle of reversibility can be expressed mathematically in two ways, namely

$$\text{a)}\quad r'_R t'_R + t'_R r'_L = 0, \tag{9}$$

$$t'_R t'_L + r'_R r'_R = 1 \tag{10}$$

or

$$\text{b)}\quad r'^*_R t'_R + t'^*_R r'_L = 0, \tag{11}$$

$$t'^*_R t'_L + r'^*_R r'_R = 1. \tag{12}$$

r'^*_R, t'^*_R are complex conjugate quantities. According to Stokes,[7] who established the reversibility principle more than 100 years ago, only the principle (b) has a physical meaning, expressing the law of conservation of energy for the dielectric-metal boundary.

Substituting the relationships following from the reversibility principle (a),

$$r'_L = -r'_R, \tag{13}$$

$$t'_R t'_L - r'_R r'_L = t'_R t'_L + r'_R r'_R = 1 \tag{14}$$

into the general Eqs. (1) and (2) and omitting everywhere the same index R, we obtain Murmann's expressions for the reflection and transmission of light by a thin metallic layer:

$$r = \frac{r' + r'' e^{-i\varkappa}}{1 + r' r'' e^{-i\varkappa}}, \tag{15}$$

$$\mathbf{t} = \frac{\mathbf{t}'\mathbf{t}''e^{-i\frac{\mathbf{x}}{2}}}{1+\mathbf{r}'\mathbf{r}''e^{-i\mathbf{x}}}. \qquad (16)$$

The writer of the present paper had for many years bjected these formulas to criticism based on their merical checking and on considerations of energy, ich showed that the phases in these formulas are rep-sented incorrectly, and that these expressions do not rmit the description of infinitely many reflections in a n metallic layer.

If the physically correct statement of the Stokes re-rsibility principle is used, then for the complex ampli-de $\mathbf{r}'_L$ and for the complex expression $\mathbf{t}'_R\mathbf{t}'_L - \mathbf{r}'_R\mathbf{r}'_L$ we tain the relationships

$$\mathbf{r}'_L = -\mathbf{r}'^{*}_R\frac{\mathbf{t}_R}{\mathbf{t}'^{*}_R} = -\mathbf{r}'^{*}_R e^{i2\vartheta'_R}, \qquad (17)$$

$$\mathbf{t}'_R\mathbf{t}'_L - \mathbf{r}'_R\mathbf{r}'_L = \frac{\mathbf{t}'_R}{\mathbf{t}'^{*}_R} = e^{i2\vartheta'_R}. \qquad (18)$$

Substituting Eqs. (17) and (18) into the general equa-ns (1) and (2), we have the expressions (omitting erywhere the same index R):

$$\mathbf{r} = re^{i\delta} = \frac{\mathbf{r}' + \mathbf{r}''e^{i2\vartheta'}e^{-i\mathbf{x}}}{1+\mathbf{r}'^{*}\mathbf{r}''e^{i2\vartheta'}e^{-i\mathbf{x}}} = \frac{r'e^{i\delta'} + r''e^{i\delta''}e^{-i\mathbf{x}}}{1+r'e^{-i\delta'}r''e^{i\delta''}e^{-i\mathbf{x}}}, \qquad (19)$$

$$\mathbf{t} = te^{i\delta} = \frac{\mathbf{t}'\mathbf{t}''e^{-i\frac{\mathbf{x}}{2}}}{1+\mathbf{r}'^{*}\mathbf{r}''e^{i2\vartheta'}e^{-i\mathbf{x}}} = \frac{t'e^{i\delta'}t''e^{i\delta''}e^{-i\frac{\mathbf{x}}{2}}}{1+r'e^{-i\delta'}r''e^{i\delta''}e^{-i\mathbf{x}}}, \qquad (20)$$

which we have combined the phase $\bar{\delta}''$ of the complex mplitude $\mathbf{r}'' = r''e^{i\bar{\delta}''}$ and the phase $2\vartheta'$ into one phase $= \bar{\delta}'' + 2\vartheta'$.

The phase shift in Eqs. (15) and (16), (19) and (20) ill in the general case be a complex number $\mathbf{x} = x - ix'$, here

$$x = \frac{2\pi}{\lambda}2n_1d_1 \qquad (21)$$

the phase shift proper, and the expression

$$x' = \frac{2\pi}{\lambda}2k_1d_1 \qquad (22)$$

connected with the damping of the light amplitude ring the passage through the thin metallic layer.

If Eqs. (19) and (20) are multiplied by their complex njugates, we obtain for the reflectance of a thin metallic yer

$$\rho = r^2 = \frac{r'^2 + r''^2e^{-2x'} + 2r'r''e^{-x'}\cos(x+\delta'-\delta'')}{1+r'^2r''^2e^{-2x'} + 2r'r''e^{-x'}\cos(x+\delta'-\delta'')}, \qquad (23)$$

ad for its transmittance

$$\tau = \frac{n}{n_0}t^2 = \frac{n}{n_0}\frac{t'^2t''^2e^{-x'}}{1+r'^2r''^2e^{-2x'} + 2r'r''e^{-x'}\cos(x+\delta'-\delta'')}. \qquad (24)$$

If the metallic layer is strongly absorbing (for in-tance, Ag, Au, Al, etc.), then there is practically only ne light reflection. From Eqs. (19) and (20), which are btained by summation of an infinite series, we take in his case only the first term. Then we obtain the follow-ng expressions:

$$\mathbf{r} = re^{i\delta} = \mathbf{r}' + \mathbf{r}''_1e^{-i\mathbf{x}} = r'e^{i\delta'} + r''_1e^{i\delta''_1}e^{-i\mathbf{x}}, \qquad (25)$$

$$\mathbf{t} = te^{i\delta} = \mathbf{t}'\mathbf{t}''_1e^{-i\frac{\mathbf{x}}{2}} = t'e^{i\delta'}t''_1e^{i\delta''_1}e^{-i\frac{\mathbf{x}}{2}}. \qquad (26)$$

The complex amplitudes $\mathbf{r}''_1 = \mathbf{r}''_1e^{i\delta''_1}$ and $\mathbf{t}''_1 = \mathbf{t}''_1e^{i\vartheta''_1}$ in Eqs. (25) and (26) assume different values than in Eqs. (19) and (20). In order to distinguish them, they are supplied with the index 1.

After multiplying the last two expressions by their complex conjugates, we obtain for the reflectance of a thin, strongly absorbing metallic layer

$$\rho = r^2 = r'^2 + r''^2_1e^{-2x'} + 2r'r''_1e^{-x'}\cos(x+\delta'-\delta''_1) \qquad (27)$$

and for its transmittance

$$\tau = \frac{n}{n_0}t^2 = \frac{n}{n_0}t'^2t''^2_1e^{-x'}. \qquad (28)$$

REFLECTION OF LIGHT BY A THIN METALLIC LAYER PLACED ON ANOTHER METAL

We have presented in the introduction the basis for the derivation of an expression for the reflection of light by a thin metallic layer placed upon a substrate of another metal. In this case it is also necessary to distinguish two possibilities: (a) the thin layer absorbs so little light that one has to consider an infinite number of reflections, and (b) the thin layer absorbs strongly, so that only one reflection of light may be considered.

We shall deal with these two cases separately.

(a) A weakly absorbing layer (for instance, a semiconducting one) is placed on a metallic substrate.

For the reflection of light by a layer of the type under consideration Eq. (19) holds, and for its reflectance Eq. (23) holds. The calculations are exactly the same as in the case of light reflection by a thin metallic layer, except for the calculation of the complex amplitude $\mathbf{r}'' = r''e^{i\delta''}$; the latter has to be calculated from the requirement that for a zero thickness of this absorbing layer the light reflection must be the same as in the case of a pure metallic substrate without any thin surface layer. For $d_1 = 0$, we have also $\mathbf{x} = x' = 0$, and Eq. (19) takes the form

$$\mathbf{r}_0 = r_0e^{i\delta_0} = \frac{r'e^{i\delta'} + r''e^{i\delta''}}{1+r'e^{-i\delta'}r''e^{i\delta''}}, \qquad (29)$$

where $\mathbf{r}_0$ is the complex amplitude of light reflected by a pure metallic substrate, of which the complex index of refraction is $\mathbf{n} = n - i\kappa$. The equation

$$r_0e^{i\delta_0} = \frac{\mathbf{n}-n_0}{\mathbf{n}+n_0}, \qquad (30)$$

also holds, where $\mathbf{r}_0$ is given by the relationship

$$r_0^2 = \frac{(n-n_0)^2+\kappa^2}{(n+n_0)^2+\kappa^2} \qquad (31)$$

and

$$\tan\delta_0 = \frac{-2n_0\kappa}{n^2+\kappa^2-n_0^2}. \qquad (32)$$

From Eq. (29) we obtain the complex amplitude $r''e^{i\delta''}$ as

$$r''e^{i\delta''} = \frac{r_0e^{i\delta_0} - r'e^{i\delta'}}{1-r_0r'e^{i(\delta_0-\delta')}}. \qquad (33)$$

This gives the relationships

$$r''^2 = \frac{r_0^2 + r'^2 - 2r_0r'\cos(\delta_0-\delta')}{1+r_0^2r'^2-2r_0r'\cos(\delta_0-\delta')}, \qquad (34)$$

$$\tan\delta'' = \frac{r_0\sin\delta_0 - r'(1+r_0^2)\sin\delta' + r_0r'^2\sin(2\delta'-\delta_0)}{r_0\cos\delta_0 - r'(1+r_0^2)\cos\delta' + r_0r'^2\cos(2\delta'-\delta_0)}. \qquad (35)$$

From the last two equations, r'' and $\tan\delta''$ can be calculated even for the most general case. It is convenient to calculate the complex amplitude $r''e^{i\delta''}$ for the normal incidence of light on a thin metallic layer, placed upon another metal, directly from the equation

$$r''e^{i\delta''} = \frac{n-n_1}{n+n_1^*}\,\frac{n_1^*+n_0}{n_1+n_0} = r''e^{i\delta''}\cdot e^{i2\vartheta'}. \tag{36}$$

For r''^2 the equation

$$r''^2 = \frac{(n-n_1)^2+(\varkappa-\varkappa_1)^2}{(n+n_1)^2+(\varkappa-\varkappa_1)^2} \tag{37}$$

holds, and for the phases $\bar{\delta}''$ and ϑ' we obtain

$$\tan\bar{\delta}'' = \frac{-2n_1(\varkappa-\varkappa_1)}{n^2-n_1^2+(\varkappa-\varkappa_1)^2}, \tag{38}$$

$$\tan\vartheta' = \frac{\varkappa_1}{n_1+n_0}. \tag{8a}$$

The phase δ'' is given by $\delta'' = \bar{\delta}'' + 2\vartheta'$.

Thus we have determined all the quantities needed for the calculation of the reflectance of a thin metallic layer placed on a metallic substrate.

(b) A thin, strongly absorbing layer is placed upon a metallic substrate. The absorption in a thin layer of such metals as, for instance, Ag, Au, Al, etc., is so strong that, for practical purposes, one can limit oneself to the consideration of only one reflection of light by the thin layer. For the reflection of light by such a layer, Eq. (25) is fulfilled, and for its reflectance Eq. (27) holds. We shall again calculate the complex amplitude $r_1'' = r_1''e^{i\delta_1''}$ from the requirement that the reflectance will be the same for the zero thickness of a thin metallic layer as for a pure substrate. For $d_1 = 0$, we have $x = x' = 0$. Substituting this result into Eq. (25), we get

$$r_0e^{i\delta_0} = r'e^{i\delta'} + r_1''e^{i\delta_1''}, \tag{39}$$

where $r_0e^{i\delta_0}$ is the reflectance of a pure substrate given by Eq. (30). From Eq. (39) we obtain

$$r_1''e^{i\delta_1''} = r_0e^{i\delta_0} - r'e^{i\delta'}, \tag{40}$$

from which it follows that

$$r_1''^2 = r_0^2 + r'^2 - 2r_0r'\cos(\delta'-\delta_0), \tag{41}$$

$$\tan\delta_1'' = \frac{r_0\sin\delta_0 - r'\sin\delta'}{r_0\cos\delta_0 - r'\cos\delta'}. \tag{42}$$

Thus, all the quantities necessary for the calculation are determined.

CONCLUSION

It remains to answer the question, In what cases may one, for the calculation of the reflectance, use the expression which is the sum of an infinite geometric series and when may one use only the first term? The reflectanc calculations carried out by the writer for a thin metallic layer demonstrate that for semiconducting layers with $n_1 > 3$ and $\kappa_1 < 1.2$, infinitely many reflections in the layer must be assumed. However, for the metals Ag, Au, Al one may assume in most cases one reflection at the thin metallic layer. In these cases the results of the calculations agree best with the experimental data.

The derivation of equations for the reflection of light at a thin metallic layer, placed on another metal, by considering two or three terms of the geometric series, is very difficult, as was shown by the writer earlier.[4] For an experimental test it is further necessary to take into account that the structure of the thinnest metallic layers depends strongly on their thickness, as was shown by Rozenberg[8] in his microtheory.

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ACCURACY OF DETERMINING OPTICAL CONSTANTS OF ABSORBING SUBSTANCES BY REFLECTION IN AN ARRANGEMENT USING A POLARIZER AND ANALYZER

A. P. Prishivalko (pp. 248-258)

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A study is made of the errors arising in several variants of a method proposed by Beattie and Conn for determining optical constants. These variants are compared with each other and with the method of Šimon.

The method of determining optical constants of absorbing substances proposed by Beattie and Conn[1] is based on measuring the coefficient of reflection of plane polarized light from the test sample with an arbitrary angle of incidence and different orientations of the polarizer and analyzer. This method is a modification of a method of Drude convenient for work in the infrared region of the spectrum. Drude's method involves measurements at the principal angle of incidence, which is close to 90 deg for strongly absorbing substances (particularly in the infrared region), and assumes the use of compensators which do not exist in the infrared region. The method under consideration here permits satisfactory results to be obtained at angles of incidence smaller than the principal angle. Determination of the relative phase difference of the components of the reflected light is accomplished indirectly through measurements of the intensity for particular positions of the polarizer and analyzer.

The method of Beattie and Conn was developed in the works of Beattie[2] and Bakhshiev,[3] where several possible variants of its practical application were proposed. It seems appropriate to examine in more detail the accuracy of these variants and to compare them with each other and with other methods of determining the optical constants of absorbing substances. At the same time we shall study the accuracy of a method for determining optical constants with the help of the Stokes parameters of the reflected light,[4] the experimental part of which is close to Beattie's variant.[2]

As in all other methods of determining the optical constants based on reflection measurements, the equations of Fresnel*

*The negative sign for the reflection coefficient of the s component is adopted for the reasons given in refs. 2, 5, and 6. With this convention the phase difference Δ is always negative.

$$r_s = -a_s \frac{\sin(\varphi - \varkappa)}{\sin(\varphi + \varkappa)}, \tag{1a}$$

$$r_p = -a_p \frac{\tan(\varphi - \varkappa)}{\tan(\varphi + \varkappa)}. \tag{1b}$$

are used in developing formulas for use in calculations.

If the incident light is linearly polarized with the plane of polarization at 45 deg from the plane or incidence, then $a_p = a_s$ and

$$\frac{r_p}{r_s} = \frac{\cos(\varphi + \varkappa)}{\cos(\varphi - \varkappa)} = \rho e^{i\Delta}. \tag{2}$$

Simple transformations of (1) and (2) yield the following relations:

$$\frac{n^2 - \varkappa^2 - \sin^2\varphi}{\sin^2\varphi \tan^2\varphi} = \frac{(1-\rho^2)^2 - 4\rho^2 \sin^2\Delta}{(1 - 2\rho\cos\Delta + \rho^2)^2}, \tag{3a}$$

$$\frac{2n\varkappa}{\sin^2\varphi \tan^2\varphi} = -\frac{4\rho(1-\rho^2)\sin\Delta}{(1 - 2\rho\cos\Delta + \rho^2)^2}. \tag{3b}$$

Under the condition

$$|(n - i\varkappa)^2| \gg \sin^2\varphi \tag{4}$$

the well known relations of Drude are obtained:

$$\frac{n}{\sin\varphi\tan\varphi} \cong \frac{1-\rho^2}{1 - 2\rho\cos\Delta + \rho^2}, \tag{5a}$$

$$\frac{\varkappa}{\sin\varphi\tan\varphi} \cong -\frac{2\rho\sin\Delta}{1 - 2\rho\cos\Delta + \rho^2}. \tag{5b}$$

If the Stokes parameters of the reflected light[4] are used to find the optical constants, and (4) holds, the corresponding formulas are:

$$\frac{n}{\sin\varphi\tan\varphi} \cong -\frac{P_1}{1 - P_2}, \tag{6a}$$

$$\frac{\varkappa}{\sin\varphi\tan\varphi} \cong \frac{\sqrt{1 - P_1^2 - P_2^2}}{1 - P_2}. \tag{6b}$$

Here P_1 and P_2 are respectively the ratios of the Stokes parameters S_2/S_1 and S_3/S_1.[4,7] From (3), (5), and (6) it is clear that experimentally the problem reduces to the determination of either ρ and Δ or P_1 and P_2.

The transmission behavior of the polarizer-sample-analyzer system of Fig. 1 is governed by the relation[8]:

$$I = I_0 \left(R_s \sin^2\Psi_P \sin^2\Psi_A + R_p \cos^2\Psi_P \cos^2\Psi_A + \frac{1}{2}\sqrt{R_s R_p}\sin 2\Psi_P \sin 2\Psi_A \cos\Delta \right), \tag{7}$$

where I_0 is the intensity of the incident light, I the intensity of the light after passage through the system, $R_s = |r_s|^2$, $R_p = |r_p|^2$, $\rho = \sqrt{R_p/R_s}$, and Ψ_P and Ψ_A are the azimuth angles of polarizer and analyzer.

Equation (7) is symmetrical in the quantities Ψ_P and Ψ_A; i.e., the analyzer and polarizer are interchangeable. This property is useful for avoiding errors due to polari-

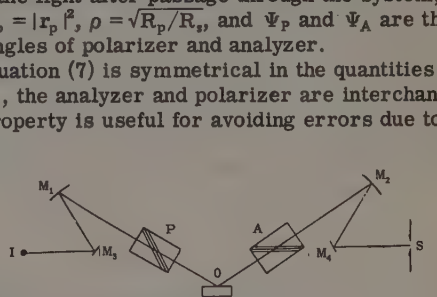

Fig. 1. Experimental arrangement for measuring optical constants according to the method of Beattie and Conn. I—light source; M_1, M_2—spherical mirrors; M_3, M_4—plane mirrors; P—polarizer; A—analyzer; S—entrance slit of monochromator; O—sample.

cation of light by the monochromator, brought about by the mounting of analyzer A, which is located between the test sample and the monochromator in a particular position. This can change the azimuth angle of the polarizer P.

If the azimuth angle of the analyzer is held fixed at $\Psi_A = 45$ deg, and the intensity of the reflected light is measured at different azimuth angles of the polarizer, then

$$I = I_0 \frac{R_0}{2} (\sin^2 \Psi_P + \rho^2 \cos^2 \Psi_P + \rho \sin 2\Psi_P \cos \Delta). \quad (7a)$$

For convenience in considering the different variants of the method, we introduce the following notation:

$$\left.\begin{aligned} I_1 &= I(\Psi_P = 0^\circ) = I_0 \frac{R_0}{2} \cdot 1, \\ I_2 &= I(\Psi_P = 90^\circ) = I_0 \frac{R_0}{2} \cdot \rho^2, \\ I_3 &= I(\Psi_P = 45^\circ) = I_0 \frac{R_0}{2} \cdot \frac{1}{2} (1 + \rho^2 + 2\rho \cos \Delta), \\ I_4 &= I(\Psi_P = -45^\circ) = I_0 \frac{R_0}{2} \cdot \frac{1}{2} (1 + \rho^2 - 2\rho \cos \Delta), \\ I_5 &= I(\Psi_P = \varphi_0) = I_0 \frac{R_0}{2} \cdot 2 \sin^2 \varphi_0 (1 + \cos \Delta), \\ I_6 &= I(\Psi_P = -\varphi_0) = I_0 \frac{R_0}{2} \cdot 2 \sin^2 \varphi_0 (1 - \cos \Delta), \end{aligned}\right\} \quad (8)$$

where

$$\varphi_0 = \arctan \rho = \arctan \sqrt{\frac{I_2}{I_1}}.$$

The quantities I_1–I_6, determined directly from measurement, are related to φ and Δ (or P_1 and P_2) through Eqs. (3), (5), and (6). From (3), (5), (6), and (8), it is possible to obtain expressions for each variant of the method which connect n and κ directly with measured values of intensity.

We shall designate the left-hand sides of (3a) and (3b) by X and Y respectively, and the left-hand sides of (5a) and (5b) by A and B. It is not difficult to see that for maximum generality it is convenient to consider not the errors in determining the index of refraction n or the index of absorption κ, but instead the errors in the directly related quantities A, B, X, and Y. We recall that the expressions (3a) and (3b) are exact, while (5a) and (5b) are approximate, so that

$$X = A^2 - B^2 = \frac{1}{\cos^2 \varphi}, \quad (9a)$$

$$Y = 2AB. \quad (9b)$$

Thus, from the magnitudes of A and B and their errors, it is possible to find the values and errors of X and Y. Moreover it is possible to find the magnitude of the errors in the determination of n and κ from the errors in A and B or X and Y. In connection with this, it is useful to keep in mind that if $\varphi = 51^\circ 50'$, then $\sin \varphi \tan \varphi = 1$ and consequently, $A = n$, and $B = \kappa$.

In order to compare the different variants of the method, expressions for A and B have been obtained in terms of measured quantities.

1. BEATTIE'S VARIANT

Measured quantities: I_0, I_1, I_3, I_4.

$$A = \frac{(I_3 - I_1)(I_3 - I_4)}{2I_3(I_1 - I_4)}, \quad (10a)$$

$$B = \frac{\sqrt{4I_1I_3(I_3 - I_4)^2 - (I_1 - I_4)^2(I_3 - I_4)^2}}{2I_3(I_1 - I_4)} \quad (10b)$$

2. VARIANT BASED ON THE STOKES PARAMETERS

Measured quantities: I_0, I_1, I_3.

$$A = \frac{I_1 - I_3}{I_1 + I_3 - I_0}, \quad (11a)$$

$$B = \frac{\sqrt{4I_1I_3 - (I_1 - I_3)^2 - (I_1 + I_3 - I_0)^2}}{2(I_1 + I_3 - I_0)}. \quad (11b)$$

3. BAKISHIEV'S VARIANT (a)

Measured quantities: I_0, I_1, I_2, I_3.

$$A = \frac{(I_3 - I_1)(I_3 - I_2)}{(I_1 + I_2)(I_3 + I_2) - 2\sqrt{I_1I_2}(I_3 - I_2)}, \quad (12a)$$

$$B = \frac{4\sqrt{I_1I_2}(I_3 - I_2)}{(I_1 + I_2)(I_3 + I_2) - 2\sqrt{I_1I_2}(I_3 - I_2)}. \quad (12b)$$

4. BAKISHIEV'S VARIANT (b)

Measured quantities: I_0, I_1, I_3.

$$A = \frac{I_3 - I_1 - 2I_2}{2I_0}, \quad (13a)$$

$$B = \frac{\sqrt{4I_0(I_0 + I_1 - I_3) - (I_1 - I_3)^2}}{2I_0}. \quad (13b)$$

5. BAKISHIEV'S VARIANT (c)

Measured quantities: I_0, I_4, and β, the azimuth angle of the polarizer at which the transmission of the polarizer-sample-analyzer system reaches a maximum.

$$A = \frac{I_0 - I_4 \cos 2\beta}{2I_4}, \quad (14a)$$

$$B = \frac{\sqrt{4I_4(I_0 - I_4) - I_4^2 \cos^2 2\beta}}{2I_4}. \quad (14b)$$

Let us assume that the absolute errors of the intensity measurements (I_0, I_1, etc.) under the conditions of the experiment are approximately the same and equal to δI. Then the ratio $\delta I / I_0$ will be the same for all variants and the error formulas for all variants (except variant 5) may be put into the form

$$\frac{\delta A}{A} = \pm \frac{\delta I}{I_0} \frac{1}{K_A} F(\ldots \cos \Delta) = \pm \frac{\delta I}{I_0} \frac{1}{K_A} f(n, \kappa). \quad (15)$$

For variant 5

$$\frac{\delta A}{A} = \pm \left\{ \frac{\delta I}{I_0} \frac{1}{K_A} F_{(5)}(n, \cos \Delta) + \frac{\delta \beta}{K_A} f(n, \cos \Delta) \frac{\partial \Delta}{\partial \beta} \right\}$$

$$= \pm \left\{ \frac{\delta I}{I_0} \frac{1}{K_A} f_{(5)}(n, \kappa) + \frac{\delta \beta}{K_A} f(n, \kappa) \frac{\partial \Delta}{\partial \beta} \right\}. \quad (16)$$

Expressions for the error δB, B are analogous.

On the basis of computed values of δA, A and δB, B we now analyze and compare all the variants. Graphical results are shown in Figs. 2 and 3. For plotting purposes it was assumed that $\delta I / I_0 = 0.005$, and the angle of incidence φ was taken to be 70°. For variant 5, which involved measurement of the angle β as well as of the intensities I_0 and I_4, the analyzer error was taken as $\delta\beta = 0^\circ 30' \approx 0.009$.

Figure 2a shows the dependence of δA, A on n for $B = 1.0$ ($\kappa = 2.563$). Figs. 2b, 2c, and 2d correspond to $B = 2$, 3, and 4, respectively ($\kappa = 5.164$, 7.746, 11.328). The numbering of the curves corresponds to the numbering of the variants under consideration. Since

$$\frac{\delta n}{n} = \pm \left\{ \frac{\delta A}{A} - \frac{1 + \cos^2 \varphi}{\sin^2 \varphi \cos \varphi} \delta \varphi \right\},$$

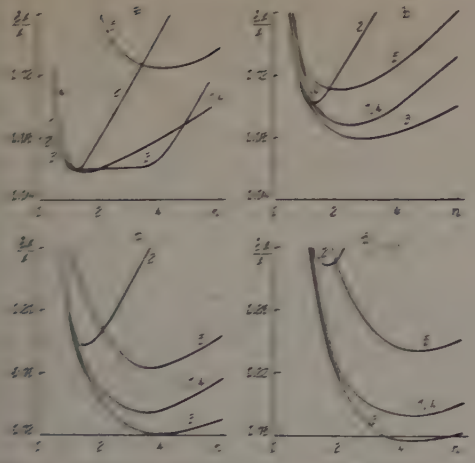

Fig. 2. Curves of δA/A vs. n. Values of κ: a—2.582; b—5.164; c—7.746; d—10.328.

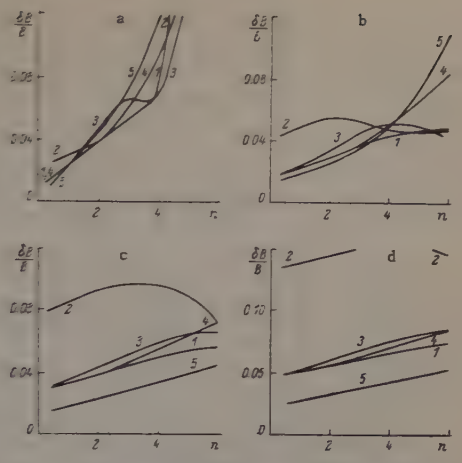

Fig. 3. Curves of δB/B vs. n. Values of κ noted in caption of Fig. 2.

, from the value of the error $\delta\varphi$ in a particular ex- ment, it is easy to find $\delta n/n$ ($\delta\kappa/\kappa$ is analogously ected with $\delta B/B$). If $\delta\varphi$ is less than 0.001, then sufficient exactness we may take $\delta A/A \cong \delta n/n$ and $\cong \delta\kappa/\kappa$.

We note that all the curves in Fig. 2 have minima ch with increasing absorption move towards larger es of the refractive index and become less deep. An ease in κ involves a considerable reduction in the racy of a determination of the index of refraction. values of the indices of absorption and refraction idered here, use of variant 3 gives the best results. ants 1 and 4 have values of error which are prac- ly equal to each other in all ranges. All variants large errors in the determination of the refractive x for $n < 1$. It should be kept in mind that if $n^2 +$ 10 formulas (5a) and (5b) are only rough approxi- ons. In this range it is necessary to use formulas and (3b).

The sizes of the errors obtained in this case are n in Table 1. Calculations show that for $0.6 \leq n \leq$ and $0.2 \leq \kappa \leq 1.4$ the errors of variants 1 and 4 practically identical.

Figure 3 represents the dependence of δB/B on n $\kappa = 2.582$, 5.164, 7.746, and 10.328. Increasing n s to increasing δB/B. This increase is particularly p for $\kappa = 2.582$ and for still smaller values of ab- tion. With growth of κ the curves become smoother, their slope decreases. The errors in variants 1, 3, 4 differ but little, and for some values of n actually cide. At smaller values of κ (not shown in the draw- the errors in all five variants turn out to be close in nitude. Although increases in κ and n lead to greater or in determining the index of absorption, for large κ the error cannot exceed 5% (with use of variant 5). This variant proves to be the most accurate for determining large values of κ. However, from a comparison of Figs. 2 and 3, we see that variant 5 is not the best for determining the refractive index.

As for the variant which simultaneously gives the most satisfactory results for both the refractive index and the absorptive index, variant 1 is indicated. Table 2 applies to this variant, where the values of $\delta n/n$ and $\delta\kappa/\kappa$ were obtained on the basis of the above-mentioned assumptions. We can see from Table 2 that an increase in n leads to an increase in the error $\delta\kappa/\kappa$. This effect is stronger at small values of κ and weaker at large ones. The error $\delta\kappa/\kappa$ has a minimum value approximately in the region $4 \leq \kappa \leq 5$. The error $\delta n/n$ also increases strongly with the growth of κ. It also has a minimum value with respect to variation of n. This minimum lies at $n = 1.5$ for $\kappa = 3$, at $n = 2.5$ for $\kappa = 5$, etc. For large values of κ the minima are weak and move towards large n.

We examine separately the potentialities of variant 2, based on the use of Stokes parameters. The curves of δA/A vs n for this variant have a minimum whose depth at $\kappa \leq 2.582$ is the same as that of the curves corresponding to variants 1 and 4. However the width of the minimum is less than for these two variants. Thus, the region of highest accuracy for variant 2 is narrower than for the other variants. With increasing absorption the accuracy of this method rapidly deteriorates. Additional consideration shows that for not very large values of κ the errors in the determination of the refractive index for variants 2 and 1 are approximately equal. Thus, the variant based on the Stokes parameters gives the same accuracy as Beattie's variant for n and κ on the order of 0.3-1.0.

Table 1. Errors in the Determination of Values of n and κ for Variants 1 and 4 ($\varphi = 70°$, $\delta I/I_0 = 0.005$)

n	0.8				0.6				1.0				1.4			
	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)
[illegible]	[illegible]	21	[illegible]	46	0.044	22	[illegible]	15	0.068	17	0.070	7	0.064	16	0.056	4
[illegible]	[illegible]	5	[illegible]	22	0.035	18	[illegible]	16	0.054	14	0.080	8	0.072	12	0.070	5
0.8	0.068	11	0.076	36	0.102	13	[illegible]	17	0.068	11	0.090	9	0.080	10	0.084	6
1.0	0.210	21	0.162	91	0.108	12	[illegible]	18	0.100	10	0.100	10	0.090	9	0.084	6
1.2	0.276	23	0.426	213	0.126	11	0.126	21	0.108	9	0.110	11	0.096	8	0.098	7
1.4	0.252	18	[illegible]	384	0.150	10	0.150	25	0.112	8	0.120	12	0.098	7	0.098	7
[illegible]	[illegible]	14	[illegible]	309	0.204	11	0.204	34	0.136	8.5	0.130	13	0.112	7	0.112	8

Table 2. Errors in the Determination of Values of n and κ for Variant 1 ($\varphi = 70°$, $\delta I/I_0 = 0.005$)

x	3				4				5				7				10			
n	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)
0.6	0.05	8.1	0.05	1.6	—	—	0.06	1.6	—	—	0.09	1.8	—	—	0.19	2.7	—	—	0.46	4.6
0.8	0.06	7.2	0.05	1.8	0.07	9.2	0.07	1.8	0.09	11.2	0.10	1.9	0.16	20.0	0.20	2.8	—	—	0.47	4.7
1.0	0.07	6.6	0.06	2.1	0.08	8.2	0.08	1.9	0.11	10.6	0.11	2.1	0.17	17.2	0.21	3.0	—	—	0.48	4.8
1.2	0.08	6.3	0.07	2.4	0.09	7.7	0.08	2.1	0.12	9.8	0.11	2.2	0.19	15.5	0.22	3.1	—	—	0.49	4.9
1.5	0.09	6.2	0.08	2.8	0.11	7.4	0.10	2.5	0.14	9.2	0.13	2.5	0.21	14.0	0.22	3.2	0.37	24.5	0.51	5.1
1.8	0.11	6.3	0.10	3.2	0.13	7.4	0.11	2.7	0.16	8.9	0.14	2.7	0.24	13.3	0.24	3.4	0.40	22.1	0.52	5.2
2.0	0.13	6.4	0.11	3.5	0.15	7.5	0.12	2.9	0.18	8.8	0.14	2.8	0.26	13.0	0.25	3.5	0.42	21.2	0.53	5.3
2.4	0.16	6.7	0.12	4.0	0.18	7.6	0.14	3.4	0.21	8.7	0.16	3.1	0.30	12.4	0.26	3.7	0.48	20.0	0.55	5.5
3.0	0.21	7.1	0.14	4.8	0.24	7.9	0.16	3.9	0.26	8.8	0.18	3.6	0.36	12.0	0.28	4.0	0.58	19.0	0.58	5.8
3.5	0.26	7.5	0.16	5.4	0.29	8.4	0.18	4.4	0.32	9.2	0.20	3.9	0.45	11.9	0.30	4.3	0.66	18.8	0.61	6.1
4.0	0.32	8.1	0.19	6.4	0.36	9.0	0.19	4.8	0.39	9.8	0.22	4.3	0.49	12.3	0.32	4.6	0.74	18.5	0.63	6.3
4.5	0.40	8.8	0.22	7.5	0.43	9.6	0.20	5.1	0.48	10.6	0.23	4.5	0.58	12.9	0.34	4.8	0.83	18.5	0.66	6.6
5.0	0.47	9.4	0.27	9.0	0.52	10.3	0.21	5.3	0.57	11.3	0.23	4.6	0.68	13.6	0.35	5.0	0.94	18.7	0.68	6.8
5.5	0.56	10.1	0.34	11.3	0.61	11.0	0.22	5.5	0.66	12.0	0.24	4.7	0.79	14.3	0.36	5.1	1.05	19.0	0.70	7.0
6.0	0.64	10.7	—	—	0.70	11.6	0.22	5.6	0.76	12.6	0.24	4.8	0.89	14.9	0.36	5.2	1.16	19.4	0.71	7.1

Practical utilization of this variant is advantageous when a special arrangement for the measurement of the Stokes parameters[9] is available.

From what has been said above it follows that among the variants of Beattie and Conn's method studied, variant 1, because of its accuracy, turns out to be the most satisfactory in the overhwhelming majority of cases. By detailed analysis of the error of this variant, regions of n and κ are found within which these quantities may be determined without the error exceeding a specified maximum. These regions (for $\delta I/I_0 = 0.005$) are depicted in Fig. 4, from which it is clear that, with the given method, the index of absorption κ can be determined with an error not exceeding 5% in the region between the curves marked 1. In the shaded region above curve 2 the error in the determination of κ does not exceed 7.5%. In the corresponding region above curve 3, $\delta\kappa/\kappa \leq 10\%$. Curve 2a bounds the region (shaded on the diagram) where the refractive index n can be determined with an error not larger than 7.5%; curve 3a corresponds to $\delta n/n = 10\%$.

Regions with the double shading contain values of n and κ which can be determined simultaneously with identical errors not exceeding 7.5% (Fig. 4a) or 10% (Fig. 4b).

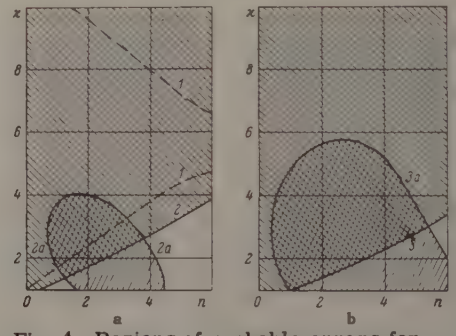

Fig. 4. Regions of probable errors for $\delta I/I_0 = 0.005$ and $\varphi = 70°$. Values of $\delta\kappa/\kappa$ and $\delta n/n$ (in %): curve 1—5; curves 2, 2a—7.5; curves 3, 3a—10.

If the error of the experiment turns out to be, for example, twice as much ($\delta I/I_0 = 0.01$), then the errors $\delta\kappa/\kappa$ and $\delta n/n$ corresponding to the curves in Fig. 4 also hav to be doubled. It is necessary to keep in mind that each curve indicates only the upper limit of the probable er-

Table 3. Errors in the Determination of Values of n and κ for Šimon's Method ($\varphi_1 = 20°$, $\varphi_2 = 70°$, $\delta R = 0.005$)

x	0.2				0.6				1.0				1.4			
n	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)
0.4	0.007	1.7	0.008	4.0	0.006	1.5	0.018	3.0	0.008	2.0	0.031	3.1	0.012	3.0	0.045	3.2
0.6	0.011	1.9	0.015	7.5	0.008	1.3	0.021	3.5	0.001	1.8	0.028	2.8	0.016	2.7	0.044	2.9
0.8	0.016	2.0	0.034	17.0	0.014	1.6	0.026	4.3	0.016	2.0	0.027	2.7	0.020	2.5	0.036	2.6
1.0	0.090	9.0	0.039	19.5	0.022	2.2	0.028	4.7	0.022	2.2	0.027	2.7	0.027	2.7	0.034	2.4
1.2	0.116	9.7	—	—	0.038	3.2	0.029	4.9	0.030	2.5	0.025	2.5	0.034	2.8	0.033	2.3
1.4	0.080	5.7	—	—	0.052	3.7	0.033	5.5	0.040	2.9	0.023	2.3	0.044	3.1	0.029	2.1
1.6	0.061	3.8	—	—	0.051	3.2	0.040	6.7	0.050	3.2	0.028	2.8	0.054	3.4	0.027	1.9
2.0	0.068	3.4	—	—	0.069	3.6			0.072	3.7	0.042	4.2	0.078	3.9	0.033	2.3
2.4	0.093	3.9	—	—	0.095	4.0			0.099	4.2	—	—	0.106	4.4	—	—

x	1.8				2.0				2.5				3.0			
n	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)	δn	$\frac{\delta n}{n}$ (%)	$\delta\kappa$	$\frac{\delta\kappa}{\kappa}$ (%)
0.4	0.018	4.5	0.070	3.9	0.022	5.4	0.093	4.7	0.032	8.0	—	—	0.045	11.3	—	—
0.8	0.027	3.4	0.051	2.9	0.032	3.9	0.063	3.2	0.043	5.4	0.097	3.9	0.058	7.8	—	—
1.2	0.041	3.4	0.046	2.6	0.045	3.8	0.056	2.8	0.060	5.0	0.079	3.2	0.078	6.5	0.130	4.4
1.6	0.061	3.8	0.039	2.2	0.066	4.1	0.050	2.4	0.083	5.2	0.069	2.8	0.103	6.4	0.113	3.8
2.0	0.086	4.3	0.032	1.8	0.092	4.6	0.036	1.8	0.109	5.5	0.055	2.2	0.141	7.1	0.100	3.4
2.4	0.115	4.8	0.047	2.6	0.123	5.1	0.041	2.1	—	—	0.040	1.6	—	—	0.089	3.0

This means that outside curve 3 or 3a it is possible r certain conditions to get entirely accurate values, hat the probability of this is rather small.

For carrying out measurements it is very important ow in what region one or the other method of deter- ng optical constants gives the best results. For this necessary to be able to compare results obtained by ous methods and to have information about the ac- cy of each. In the present work we have carried out comparison of variant 1 (or of variant 4, which is tically the same) with the well known method of on.[10,11] The comparison is based on errors which e in the treatment of the experimental data. In all s the experimental error is assumed identical. It ld be noted that Šimon's method requires the use of lute measurements of the reflection coefficient. this method it is more difficult to obtain the same ee of experimental accuracy as, for example, with tie's method, in which relative measurements are e.

In Table 3 are shown data concerning the magnitude e errors in Šimon's method. The table corresponds e best variant of this method, when the incident light ane polarized with the electric vector in the plane cidence.

The error of the experiment is assumed to be $\delta R = 5$, which corresponds to the error assumed in the ideration of Beattie's method. For values of n and ceeding those shown in Table 3, a very rapid growth e errors takes place and the accuracy of the method ngly deteriorates.

From comparison of the data shown in Tables 1 and 3, llows that in the regions of n and κ considered, and r the same experimental conditions, Šimon's method gives results of higher accuracy. However, for high values of n and κ (e.g., for metals) it does not give satisfactory accuracy. Here we must give preference to the method of Beattie and Conn. The choice of variants of this method is determined by the specific conditions of the experiment.

In closing, I express my deep appreciation to B. I. Stepanov for proposing the theme and for his great interest in the work.

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PRECISION DIFFRACTION GRATINGS FOR METROLOGIC PURPOSES

G. N. Rassudova and F. M. Gerasimov (pp. 259-261)

Received 9 September 1960

This article describes a method of preparing transmission diffraction gratings by etching reflection gratings ruled on layers of aluminum by a ruling engine. Such gratings could be used for very accurate measurement of linear displacement by means of moiré bands.

In recent years, considerable interest has been shown in measuring linear displacement by means of moiré bands, which appear whenever a beam of light passes through two transmission diffraction gratings which have been superimposed in a certain manner. The theory of moiré bands as it applies to our case has been described in detail by J. Guild.[1] Relative displacement of gratings perpendicular to the lines causes a proportional shift of the moiré bands. This can be utilized to measure the displacement of the gratings.

In most cases the displacement of bands is detected by a photocell and the electrical signals counted electronically or used to operate control systems. It should be remembered that the light registered by a photocell passes through a considerable portion of the grating. This fact increases the accuracy of readings due to the averaging effect on local fringe errors. In addition, however, the progressive errors of gratings are almost fully preserved in the final reading.

Measuring by means of moiré bands has found application in a variety of automatic installations, such as metal cutting lathes with program control,[2-6] measuring microscopes, instruments for measuring the amplitude of vibration,[8] etc.

In all the abovementioned cases, the transmission gratings used have been either phase gratings with rulings having triangular[9] or rectangular[10] profiles, or amplitude gratings with "black and white" rulings.[11] The last two types are prepared photographically. These usually have less than 200 grooves per mm; the most frequently used gratings had 4 to 40 grooves per mm. Both replicas and photographic copies are subject to errors due to deformation of the material from which they are made. This, of course, limits the accuracy of measurements by moiré bands. In principle, however, this method, when used with high quality gratings, permits one to measure linear magnitudes with an accuracy equal to that obtained by ordinary interferometers.

We used the following method to prepare accurate metrological gratings. Triangular grooves were cut by a diamond point in a layer of aluminum deposited on a glass plate (see Fig. 1a). The ruling was done on a ruling engine used for the manufacture of diffraction gratings. The thickness of the aluminum layer was such that the bottom of the groove barely touched the glass base. The grating was then etched to produce transparent strips and opaque bars (Fig. 1b). In this manner, transparent strips were obtained with remarkably straight edges

Fig. 1. Cross-sectional view of ruling (a) before etching, (b) after etching.

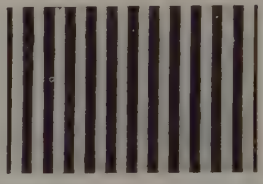

Fig. 2. Microphotograph of a transmission grating (200 lines/mm) by transmitted light (at 1300:1 magnification).

(Fig. 2). The ratio between the widths of the transparen and opaque regions was regulated by controlling the dur tion of etching, and checked by observing the zero orde transmission of the grating.

The method just described was used to prepare tra mission gratings of 200 to 1200 lines/mm, with ruled areas up to 160 mm wide. The coefficient of transmissi in the zero order of the spectrum did not vary more tha 10% over the entire area. Examination of the front of th diffracted wave by means of the interference technique showed that the etching process did not affect the accur of the grating divisions.

The transparency of a grating in any order of the spectrum (m) depends on the ratio of the transparent part (a) to the total width of the groove (d) and can be de termined by the formula

$$\tau_m = \frac{I_m}{\sum_k I_k} \cdot \frac{a}{d} .$$

The value of I_m can be calculated by the well-known for mula which determines the distribution of light intensity produced by a transmission grating.

In the type of grating under investigation, the brigh beams are those of the zero and first orders, which are also the ones used to produce moiré bands. Figure 3 is schematic diagram of the path of the light rays through two crossed gratings. The absolute value of the angle o incidence is equal to that of the angle of diffraction; thi

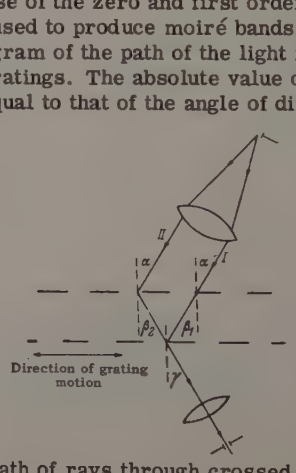

Fig. 3. Path of rays through crossed gratings.

inates the influence of the spacing between the grat-
on the position of the moiré bands.[1] Beam I is
ed as a result of the diffraction of light in the zero
r at the first grating and in the first order in the
nd grating. Beam II is formed as a result of first
r and zero order diffraction at the two gratings, re-
tively. In certain directions, in addition to the beams
n schematically, there are also beams obtained
gh the combination of other orders of diffraction.
e are less intense and therefore have little effect on
nterference bands.

The Table shows values of the transmission coeffi-
s of one grating in the zero order of the spectrum
and a system of two gratings arranged in the man-
described (τ_{01}), both calculated by means of the above
ula for various values of the ratio a/d. It can be
that the maximum transmission of the system is 8%
e original intensity of illumination, which occurs
the ratio a/d = 0.65. In view of these results,
y grating was etched until transmission in the zero
r approached 40 to 50%.

Relationship Between the Coefficient of Transmission τ and the Ratio of the Transparent Width to the Total Width of the Groove (a/d)

$\frac{a}{d}$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
τ_0 (%)	6	11	18	27	39	53	70	87
τ_{01} (%)	1	2	4	6	8	8	5	2

The light passing through such a set of gratings and
ring the field of vision includes multiple reflections
the opaque surfaces of the gratings. The intensity of these additional rays is relatively high, due to the high coefficient of reflection of the aluminum opaque strips. These reflected rays, passing through a parallel arrangement of gratings, create their own system of lines, which is superimposed upon the useful lines. In order to eliminate this superimposition, the gratings are inclined to form a wedge whose edge is perpendicular to the direction of the lines. In this manner, the spurious rays are deflected toward the base of the wedge and are then cut out by the slit located in front of the photocell.

Gratings with 1200 lines/mm, obtained by means of the abovedescribed method, were used to control an experimental ruling engine used to manufacture diffraction gratings. The accuracy of the rulings was of the order of 0.01 μ.

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SHORT COMMUNICATIONS

THE FREQUENCY DEPENDENCE OF RAMAN LINE INTENSITIES

I. I. Kondilenko and V. L. Strizhevskii (pp. 262-263)

Received 26 December 1960

As has been shown,[1] the Raman tensor components,
rmining the intensity of the scattered radiation, have
ollowing form in the adiabatic approximation

$$\alpha_{r,r\pm1} = -\frac{e^2}{\omega\omega_0}\sum_{j(j\neq 0)}{}' \left\{ \frac{2\omega'_{j0}}{\omega'^2_{j0}-\omega_0^2}\left[(S_x^{0j})_1 (S_x^{j0})_0 + (S_x^{0j})_0 (S_x^{j0})_1\right] - 2\frac{\omega'^2_{j0}+\omega_0^2}{(\omega'^2_{j0}-\omega_0^2)^2}\,|(S_x^{0j})_0|^2 \left(\frac{\partial\omega'_{j0}(Q)}{\partial Q}\right)_{Q=Q_0}\right\}(Q-Q_0)_{r,r\pm1}. \quad (1)$$

e and below we will use the same symbols as in
1.

The purpose of the present communication is to
uss some theoretical questions connected with for-
a (1), to present some experimental results of the
uency dependence, and to compare them with the
ry.

As has already been pointed out in ref. 1, formula
differs from the corresponding expression obtained
efs. 2 and 3. One must, however, refine the question of the reasons and nature of this difference. It was asserted in ref. 1 that the use of expressions, written using a vector potential and field strength, for describing the interaction of radiation with matter leads to different results for the Raman tensor. However, one can show that the series obtained for the tensor α, containing a summation over the intermediate states, are characterized in both cases by identical values of the sums (compare with ref. 4). One need only rearrange these series, writing the general term in a different form. It is understood that the speed of convergence of the two series will be different (because rearrangement of the general term of a series, as is known, changes its convergence).

Formula (1) was obtained in ref. 1 from the general expression for α by its rearrangement using the adiabatic approximation (transition to polarizability theory). Thus, the form of writing the initial expressions plays no role and all of the rearrangements can be derived identically. As a result of this the final expressions found in ref. 1, conforming to one of the expressions for α, can

also be derived easily for the case of another initial expression defining α. For this one need only make the obvious substitution of the corresponding quantities in the formulas from ref. 1. Understandably, the series obtained for α in the two cases will possess (just as the initial ones) different convergences.* Therefore it can be found that consideration of only one term (corresponding to the most significant electronic absorption band) in one of the series will already lead to a satisfactory agreement of theory with experiment, while for the series with the other formulation of the general term such an agreement is absent, i.e., the role of the rejected terms is still large. It is possible that the picture will be different for different molecules. A comparison of theory with experiment can appear quite useful for a solution of this question.

*It is of interest to evaluate the relative role of the different terms of the series mentioned (even if in an example of some model or other). However this problem goes beyond the bounds of the present communication.

The contribution of each electronic level j in expression (1) consists of two members. The first member arises on consideration of the dependence of the matrix elements S^{j0} (equal to $[i\omega'_{j0}(Q)/c]M^{j0}$) on the nuclear coordinates Q, where the splitting of the intermediate electronic states by the nuclear vibrations is neglected. The second member corresponds to a more detailed examination of the vibrational structure taking account of the mentioned splitting. From a mathematical viewpoint this resolves into taking account of the energy differences of the arbitrary and Franck-Condon transitions by a series in the frequency differences of the electronic transition and the exciting line.

It is understandable that as ω_0 recedes from the absorption band the second member in (1) should weaken. This is expressed by the fact that its dependence on ω_0 is stronger than the first member, and as a result of this it decreases faster on recession of ω_0 from ω'_{j0} (on approaching the band the second member grows faster than the first). What will be the relative role of the two members for that degree of separation which is realized in an actual experiment? General discussions do not give an answer to this question; specific estimates are necessary here. Calculations made in refs. 2 and 5 have shown that in a series of cases the second member dominates. Generally speaking, one can expect that the relative magnitude of the second member will be larger the less the molecule is "loose" (i.e., the steeper the potential energy curves of the nuclear motions) and the larger the difference of the nuclear equilibrium positions in the ground and excited electronic states. It is also evident that the indicated quantity increases on approach to absorption bands. It is possible besides that there exist molecules for which the first member of formula (1) plays a more important role.

We have carried out experimental investigations of the frequency dependence of the Raman intensity of the 656 cm^{-1} line of liquid CS_2 on excitation by the mercury lines $\lambda_c^0 = 5461$, $\lambda_e^0 = 4358$, $\lambda_k^0 = 4047$ A. This case is of interest because an electronic absorption band is located rather close (about 32,000 cm^{-1} [6]) to the exciting lines. The results are given in the Table. If, in correspondence with the conclusions of refs. 2 and 5 and the closeness of an absorption band (the influence of the others is neglected), it is assumed that the second term dominates in (1) and the intensity ratios are then calculated, we obtain the results presented in column 3. Considering the closeness of the λ_k^0 line to the absorption band one can state that the theory in the given case corresponds in general with experiment.*

*If we use an expression for α written in a form differing from (1) (cf. the above), then, for analogous assumptions, the agreement of theory and experiment is significantly worse. However, a contrary assumption regarding the relative role of the two members in the expression for α improves the agreement. Just as in ref. 1 this signifies that, for choosing between the expressions of the two forms, one must carry out measurements for substantially greater separations of the exciting lines from an absorption band.

Ratio	Experiment	Theory
$\frac{I_e}{I_c}$	4.2	4.8
$\frac{I_k}{I_c}$	8.4	11.3

In conclusion the authors thank P. A. Apanasevich f useful discussion.

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VESTIGATION OF THE INITIAL STAGES IN THE ONSET OF ELECTROLUMINESCENCE OF A ZnS:Cu:Al PHOSPHOR

P. S. Litvinova, L. P. Rabotkina, and P. E. Ramazanov (pp. 264-265)

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It is known that when an ac electric field is turned he intensity of luminescence of an electroluminor not immediately reach its steady state value.[1-3] ugh a great deal of attention has been devoted lately e study of electroluminescence, very few articles so far been devoted to an investigation of the in- ity build-up in electroluminescence. Yet a study of process at different temperatures and for different s of exciting voltage may give results which will e useful in understanding the mechanism of electro- nescence in general.

In the present paper we study the electrolumines- e build-up of a ZnS:Cu:Al phosphor excited by a soidal electric field at 40 cycles and 800 volts. Be- each experiment the phosphor was de-excited by ing to 100°C. The intensity of electroluminescence registered by a FEU-19M photomultiplier and was rded by a MPO-2 loop oscillograph. A phosphor r 0.14 mm thick was placed between mica plates out a dielectric filler. One of the electrodes was allic; the other was conducting glass.

During the period of the applied voltage, the ob- ed electroluminescent brightness pulses have two e maxima and two additional small ones. We studied behavior of the principal maximum, which always ap- s during build-up at the beginning of the second half- e of the voltage, at the instant when the voltage is e to zero. The existence of retardation was indicated viously.[2] As the build-up proceeds, the lag of the chtness wave relative to the voltage wave increases. is illustrated in Fig. 1. The number of half-periods m the onset of excitation is plotted along the abscissa. electroluminescence intensity I at the first maximum the lag $\Delta\varphi$ of this maximum relative to the voltage e in the preceding half-cycle are plotted along the or- ate axis. Figures 1a and 1b show that the phase of the imum "flares up" simultaneously with the brightness d-up of this maximum, i.e., the position of the inten- maximum shifts further relative to the beginning of half-period. At the tenth period of the applied volt- the amplitude of the brightness wave and its lag ative to the voltage wave reach a steady-state value.

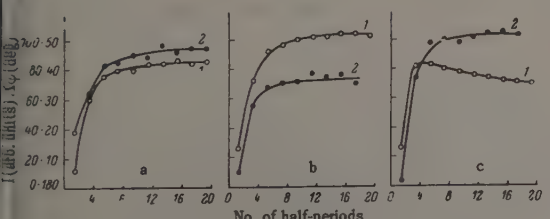

Fig. 1. Brightness change (curve 1) and phase change (curve 2) during the build-up of the principal maximum at different temperatures. Temperature (in °C): a—(−40); b—64; c—(−115).

The build-up process was studied at 27 temperatures between 113 and 430°K. In all cases we observed a parallelism between the shape and phase of the intensity build-up. On the basis of these experiments, we were able to compare the temperature dependence of intensity and phase behavior. Figure 2 shows the change in the amplitude of the ac component of the intensity of the main peak for the tenth period of the applied voltage (curve 1) and the shift in the phase of this peak relative to the voltage wave (curve 2), both being given as functions of the temperature. The figure shows that except for the low temperature range, which will be discussed below, the changes in intensity and phase follow the same course. Thus over a wide temperature range we may speak of the parallel behavior of the intensity and of its build-up time. After maintaining almost constant values between −100° and −26°C, the phase and brightness fall sharply to a minimum at −5°C. As the temperature increases further, they reach a maximum again at +58°C, after which they fall simultaneously. The minima occurring at low temperatures (−162°, −115°C) are apparently of a different origin from those occurring at high temperatures (−5°C): the brightness minimum at the high temperature is accompanied by a simultaneous sharp regression in phase, while at the low temperature the brightness minimum has almost no effect on the phase behavior. Thus, in the latter case, brightness turned out to be more sensitive than phase to a change in temperature.

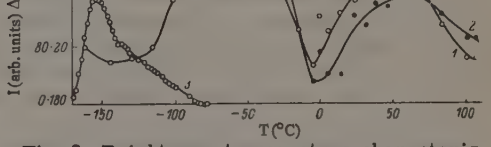

Fig. 2. Brightness-temperature characteristic (curve 1) and phase-temperature characteristic (curve 2) of the principal maximum and the glow curve (curve 3) when the phosphor is excited by an electric field at 900 volts and 40 cycles.

In order to understand the reason for the decrease in brightness at low temperatures, which is not accompanied by a marked change in phase, we investigated the thermal stimulation of the phosphor after it was excited by a field of 900 volts and 40 cycles for 2 min. The subsequent heating, without field, was carried out at the rate of 0.5°/sec (curve 3). About 3 min were required to obtain this curve, i.e., the time spent by electrons on localization levels is fairly long. On the other hand, the time interval between the instant the field is applied and the end of the tenth period, which is the interval covered by our measurements, amounts to only 0.25 sec. Thus,

under the specified conditions, the electrons moving through the lattice could be captured by trapping levels and took almost no part in the emission of radiation. This resulted in a decrease in brightness in this temperature range. As shown by experiments, the time during which brightness increased within each half-period (phase) showed almost no change. (See Fig. 2.) The capture of electrons moving through the lattice by trapping levels at low temperature was also reflected in Fig. 1c obtained at −115°C. In this case the brightness during build-up falls more and more from period to period, starting with the sixth half-period, while the phase increases as usual to higher and higher values. At −40°C (Fig. 1a) when, as seen from Fig. 2 (curve 3), the electrons are no longer localized, brightness increases as the number of half-cycles increases.

Experiments which we carried out at 160 cycles have shown that the correspondence in the time dependence of phase and brightness and the temperature dependence of phase and brightness in the tenth period are maintained. This correspondence is destroyed when the frequency is further increased to 640 cycles.

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MICROPHOTOMETRIC DETERMINATION OF THE QUANTITY OF ABSORBING MATERIAL IN INHOMOGENEOUS OBJECTS

A. I. Sherudilo and V. Ya. Brodskii (pp. 266-267)

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One of the growing trends in spectroscopy at the present time is the analysis of biological structures (animals and plant cells), with a view toward the quali tative and quantitative study of the chemical components of cells. Certain difficulties are encountered in utilizing ordinary methods of absorption spectroscopy for studying materials located in structures of microscopic size. For instance, nonuniformity in the distribution of material in the cell can lead to considerable error in the determination of optical density.[1-3] Techniques for reducing errors due to nonuniformity of distribution have been suggested in a number of papers; these consisted in effecting the greatest possible reduction in the dimensions of the photometer slit[2,4] or in representing the distribution in the form of some simple model (sphere, cylinder) and making appropriate modifications in the equations.[1,3] In contrast to previous investigators, we have found it possible to analyze the general case of a nonuniform distribution to which any inhomogeneity can be reduced.

In the general case of a nonuniform distribution of the material being measured, we have the following expression for transmission

$$\frac{\Phi}{\Phi_0}=\frac{1}{S_0}\iint\limits_{S_0} e^{-k(\lambda)\frac{dm}{dS}(x,y)}\,dS, \qquad (1)$$

where S is a surface in the object perpendicular to the incident light beam, with running coordinates x, y; S_0 is the area of the light beam in the plane S (area of the probe); Φ_0 is the incident and Φ the transmitted light flux; $K(\lambda)$ is the specific absorption index, depending on the wavelength λ; m is the quantity of material.

In the particular case of uniform distribution of mass with respect to area

$$\frac{dm}{dS}=\text{const}=\frac{m_0}{S_0}=c_0d_0,$$

where c_0 is the concentration and d_0 is the thickness of the layer of absorbing material, Eq. (1) transforms into the usual form of the Bouguer-Lambert-Beer law:

$$\frac{\Phi}{\Phi_0}=e^{-k(\lambda)c_0d_0}. \qquad (2$$

The essence of the proposed method for photometry of inhomogeneous objects is as follows: Let us expand the expression under the integral in formula (1) in a series and integrate term by term

$$\frac{\Phi}{\Phi_0}=1-k_{(\lambda)}\frac{1}{S_0}\iint\limits_{S_0}\frac{dm}{dS}\,dS+\frac{1}{2!}k_{(\lambda)}^2\frac{1}{S_0}\iint\limits_{S_0}\left(\frac{dm}{dS}\right)^2dS+\ldots+$$
$$+\frac{(-1)^n}{n!}k_{(\lambda)}^n\frac{1}{S_0}\iint\limits_{S_0}\left(\frac{dm}{dS}\right)^n dS. \qquad (3$$

Taking into account that

$$\frac{1}{S_0}\iint\limits_{S_0}\frac{dm}{dS}\,dS=\frac{m_0}{S_0},$$

and introducing the notation

$$\iint\limits_{S_0}\left(\frac{dm}{dS}\right)^2dS=P_2,\quad \iint\limits_{S_0}\left(\frac{dm}{dS}\right)^n dS=P_n,\quad 1-\frac{\Phi}{\Phi_0}=T,$$

we obtain the following expression for the transmission:

$$S_0T=k_{(\lambda)}m_0-\frac{1}{2!}k_{(\lambda)}^2P_2+\ldots+\frac{(-1)^n}{n}k_{(\lambda)}^nP_n\ldots \qquad (4$$

Since the power series obtained converges fairly rapidly, we confine ourselves to n terms of this series, where the number n is determined by the accuracy required of the calculation. By making photometric measurements of the object at several wavelengths $\lambda_1, \lambda_2, \ldots \lambda_n$, which will exhibit different specific indices of absorption $k_1, k_2, \ldots k_n$ (1, 2, ... n are the different wavelengt we obtain a system of n equations with n unknowns m_0, $P_2, P_3, \ldots P_n$; that is,

$$\left.\begin{aligned} S_0 T &= k_1 m_0 = \frac{1}{2!} k_1^2 P_2 + \ldots + \frac{(-1)^n}{n!} k_1^n P_n, \\ S_0 T_2 &= k_2 m_0 - \frac{1}{2!} k_2^2 P_2 + \ldots + \frac{(-1)^n}{n!} k_2^n P_n, \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ S_0 T_n &= k_n m_0 - \frac{1}{2!} k_n^2 P_2 + \ldots + \frac{(-1)^n}{n!} k_n^n P_n. \end{aligned}\right\} \quad (5)$$

The system of first degree equations obtained can easily solved for any values of n. Thus, for n = 2 n k_1 and k_2 known,

$$m_0 = \frac{S_0 (T_2 k_1^2 - T_1 k_2^2)}{k_2 k_1^2 - k_1 k_2^2}. \quad (6)$$

For measurements at three wavelengths (n = 3)

$$= \frac{S_0 \left[T_1 k_2^2 k_3^2 (k_2 - k_3) + T_2 k_1^2 k_3^2 (k_3 - k_1) + T_3 k_1^2 k_2^2 (k_1 - k_2) \right]}{k_1 k_2 k_3 \left[k_2 k_3 (k_2 - k_3) + k_1 k_3 (k_3 - k_1) + k_1 k_2 (k_1 - k_2) \right]}. \quad (7)$$

It is convenient for purposes of computation to de- $k_2 = \alpha k_1$ and $k_3 = \beta k_1$. Then Eqs. (6) and (7) can be resented in the form

$$m_0 = \frac{S_0 (T_2 - \alpha^2 T_1)}{k_1 (\alpha - \alpha^2)}, \quad (6')$$

$$m_0 = \frac{S_0 \left[T_1 \alpha^2 \beta^2 (\alpha - \beta) - T_2 \beta^2 (1 - \beta) + T_3 \alpha^2 (1 - \alpha) \right]}{k_1 \alpha \beta \left[\alpha^2 (\alpha - \beta) - \beta (1 - \beta) + \alpha (1 - \alpha) \right]}, \quad (7')$$

where all the quantities (except the absorption T) are calculated beforehand and substituted into the formulas as constant parameters.

A comparison of the proposed "multiwave" method with other methods of cell photometry will indicate its area of application in the spectral study of inhomogeneous objects.

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SPECTRAL TRANSMISSION AND THE INVERSE PROBLEM OF SCATTERING THEORY

K. S. Shifrin and V. F. Raskin (pp. 268-271)

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1. An approximate formula was derived in ref. 1 for scattering coefficient of a particle k as a function of dius a, wavelength λ, and relative index of refraction for the case of a particle having optical properties ich are not very different from those of its environ- nt ("soft" particles):

$$k = 2\pi a^2 \left\{ 1 - \frac{1}{\delta} \sin 2\delta \right\}, \qquad \delta = \frac{2\pi a}{\lambda} (m - 1). \quad (1)$$

This formula correctly describes the dependence of n δ when δ is large, but cannot be carried over to the yleigh case of small δ. A formula which is more gen- al than (1) is given in ref. 2:

$$k = 2\pi a^2 \left\{ 1 - \frac{1}{\delta} \sin 2\delta + \frac{1 - \cos 2\delta}{2\delta^2} \right\} = 2\pi a^2 K(\delta). \quad (2)$$

Formula (2) agrees with (1) when δ is large and ves the correct value for k when δ is small. For a dydisperse sol with a distribution curve f(a) we have

$$\bar{k}(\lambda) = \int_0^\infty k(\lambda, a) f(a)\, da. \quad (3)$$

Formula (3) is a Fredholm integral equation of the rst kind and permits us to set up the problem of deter- ining the unknown distribution curve f(a) according to e known kernel K (λ, a) and the scattering coefficient the polydisperse sol $\bar{k}(\lambda)$. The latter is determined ex- rimentally by measurement of the spectral transmis- on. Taking formula (2) for k (λ, a) we have

$$\bar{k}(\lambda) = \int_0^\infty k(\delta) 2\pi a^2 f(a)\, da. \quad (4)$$

We make the following change of variables

$$\left.\begin{aligned} \nu = \frac{1}{\lambda}, \quad \delta = 2\pi a (m - 1) \nu, \quad 2\pi a^2 f(a) = m(a), \\ \bar{k}(\lambda) = g(\nu), \quad k(\delta) = l(\nu a). \end{aligned}\right\} \quad (5)$$

Equation (4) now has the form

$$g(\nu) = \int_0^\infty l(\nu a)\, m(a)\, da. \quad (6)$$

In Eq. (6), the kernel appears as a function of the product of the variables. It is proven in the theory of integral equations that Eq. (6) can be rigorously dealt with in this case by using Mellin's transform; i.e., an exact formula (see ref. 3) is obtained for the function m(a).

Applying the Mellin transform to both sides of Eq. (6) we obtain

$$\left.\begin{aligned} G(s) = \int_0^\infty \nu^{s-1} d\nu \int_0^\infty l(\nu a)\, m(a)\, da = \int_0^\infty a^{-s} m(a)\, da \\ \times \int_0^\infty l(\nu a) (\nu a)^{s-1} d(\nu a) = M(1 - s) L(s) \end{aligned}\right\} \quad (7)$$

in which

$$\left.\begin{aligned} G(s) &= \int_0^\infty t^{s-1} g(t)\, dt, \\ L(s) &= \int_0^\infty t^{s-1} l(t)\, dt, \\ M(1 - s) &= \int_0^\infty t^{-s} m(t)\, dt. \end{aligned}\right\} \quad (8)$$

The functions G, L, and M are the Mellin transforms

for g, l, and m. From formulas (7) and (8) we have

$$M(s)=\frac{G(1-s)}{L(1-s)}. \quad (9)$$

Formulas (8) make it possible to find L and G when l(t) and g(t) are given. Knowing these functions we can use (9) to calculate the function m(s). Returning by the inverse transformation to the original function m(a), we find

$$m(a)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\frac{G(1-s)}{L(1-s)}a^{-s}ds. \quad (10)$$

Hence, for the distribution curve f(a) we have

$$f(a)=\frac{m(a)}{2\pi a^2}. \quad (11)$$

2. Let us investigate the nature of the functions $\overline{k}(\lambda)$ which are found in our problem. For example, let the microstructure of the sol be described by the formula

$$f(a)=Aa^{\mu}e^{-\gamma a}, \quad (12)$$

representing a so-called gamma-distribution with the parameter μ.

Here A is a normalization parameter (scale !), and μ and λ are parameters characterizing the shape of the distribution curve.

Let us introduce the intermediate notations

$$\left.\begin{aligned}&\varepsilon=\frac{2}{\eta}\delta,\quad \eta=\mu+1,\\ &\overline{k}_{\infty}=2\pi\overline{a}^2,\\ &\nu=\arctan\varepsilon.\end{aligned}\right\} \quad (13)$$

where $\overline{\delta}$ and $\overline{a^2}$ are mean values of the quantities δ and a^2 taken with respect to the distribution (12). Substituting (12) into (4), performing the integration, and using the notation of (13), we obtain

$$\overline{k}(\lambda)=\overline{k}_{\infty}\theta(\varepsilon), \quad (14)$$

$$\theta(\varepsilon)=1+2\frac{\Gamma(\gamma_1)}{\Gamma(\eta+2)}\cot^2\nu\{1-\cos^{\eta}\nu[\cos\eta\nu+\gamma_1\sin\nu\sin(\eta+1)\nu]\}. \quad (15)$$

The function $\theta(\varepsilon)$ is a diffraction correction for $\overline{k}_{\infty}$ (polydisperse scattering coefficient for the maximum size particles).

In the limiting case when $\varepsilon\to\infty$ and the value of θ approaches 1 we find the region of geometrical optics.

When ε is small the function $\theta(\varepsilon)$ has the form:

$$\theta(\varepsilon)=\frac{(\eta+2)(\eta+3)}{4}\varepsilon^2\left[1-\frac{\varepsilon^2}{18}(\eta+4)(\eta+5)+\ldots\right]. \quad (16)$$

We have drawn up a detailed table for determining $\theta(\varepsilon)$ at intermediate values of ε.

Curves of $\theta(\varepsilon)$, $\mu=0$, 2, 4, 6, 8, and 10 are shown in Fig. 1. It is easy to see that as μ increases, the curves have narrower and higher maxima and are displaced toward $\varepsilon=0$. At $\mu=\infty$, we go over to the monodisperse case. The $\theta(\varepsilon)$ curve now coincides with the known curve of the factor K(δ) from formula (2) for the coefficient of scattering from a single particle. The largest value of θ turns out to be 3.9; the corresponding value of ε is zero.

In the monodisperse case, the graph of the diffraction coefficient of scattering is usually constructed as a function of δ (or ρ). Transforming here from ε to $\overline{\delta}$ according to the formula

$$\delta=\frac{\eta}{2}\varepsilon,$$

we obtain the curves for $\theta(\varepsilon)$ represented in Fig. 2. It can readily be seen that as μ increases, the maximum value of θ increases and is displaced to the right. It

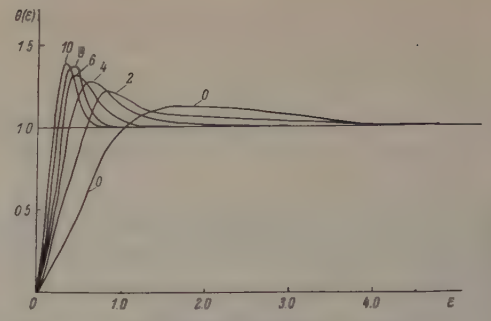

Fig. 1. The numbers near the curves are the values of μ.

takes on its maximum value of 3.9 when $\mu=\infty$ (the monodisperse case) and $\overline{\delta}=2.0$ (this value is denoted in Fig. 2 by the vertical line). It is easy to calculate the spectral transmission of aerosols of the most diverse structure using tables of $\theta(\varepsilon)$. At $\lambda=0$ (geometrical optics) all $\theta=1$; as λ increases, the curves pass through a maximum and then decline, approaching zero. Formulas of the Angstrom type

$$k\sim\lambda^{-n},\quad n=\text{const}. \quad (17)$$

are used for investigating the possibility of application in the visible and near infrared regions.

It should be noted that when $\overline{a}=0.1\ \mu$, then $\overline{\delta}=0.510$ and 0.255 correspond to values of $\lambda=0.4$ and 0.8 μ. We see from Fig. 2 that formula (17) is approximately fulfilled for all three μ, and $n\simeq 1$. As is well known, this is in good agreement with data from measurements of aerosols near the ground.[4]

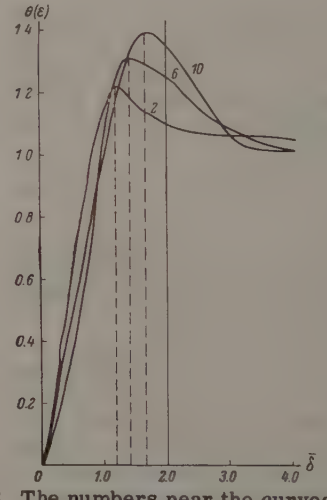

Fig. 2. The numbers near the curves are the values of μ.

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DURATION OF THE PHOTO- AND RADIOLUMINESCENCE OF ANTHRACENE AND NAPHTHALENE CRYSTALS

M. D. Galanin and Z. A. Chizhikova (pp. 271-273)

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The duration of the radioluminescence τ_r of anthracene and naphthalene crystals has been measured repeatedly in recent times in connection with their use in scintillation counters (see the review, ref. 1). The duration of photoluminescence τ_f of anthracene and other crystals has also been measured. The values of τ_r and τ_f for a number of organic crystals were first compared in ref. 2. It was found that, in general, the values of τ_r and τ_f are different, and that $\tau_r > \tau_f$ in the majority of cases. Broad conclusions were drawn about the mechanism of luminescence in the work by Birks,[3] based on the differences in the values of τ_r and τ_f. However, τ_r and τ_f were measured by substantially different methods in many of these investigations; the τ_r values were measured by observing the pulses with an oscillograph or by the method of pulse reflection with a shorted line, whereas τ_f was determined by a fluorometric (phase) method. The data on whether the decay law of the luminescence is strictly exponential are rather inconsistent. If the decay is not exponential, then the differences in method can have a substantial effect on the results.

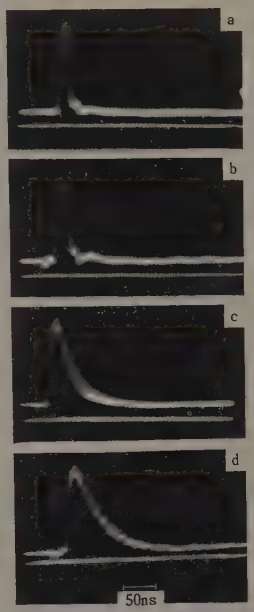
In this work, τ_r and τ_f were measured by exactly the same method, i.e. by oscillographic observation of γ-scintillation pulses and pulses excited by a brief spark. The use of an oscillograph (DESO-1) made it possible to study crystals with fairly large τ values; i.e., naphthalene and anthracene.

The photomultiplier fed directly into an RK-50 cable; the input of the oscillograph was shunted by a 150 ohm resistance, equal to the pulse impedance of the cable. The apparatus function characterizing the resolving time of the equipment was determined from the behavior of the noise pulses of the dark current corresponding to single electrons emitted by the photocathode. Of the photomultipliers at our disposal, the FEU-33 and the FEMI-6094B proved to be the best, the pulses from the latter having a somewhat steeper trailing edge (Fig. a).

The spark was produced between platinum electrodes at a voltage of about 1 kv (through a 10 megohm resistance) and was similar to the one used in ref. 4. A capacitance of 10 $\mu\mu$f was connected in parallel with the spark gap to increase the energy of the pulse. Under these circumstances, the duration of the light pulses only slightly exceeds the duration of the noise pulses (Fig. b).

The crystals were about 2 cm thick and were obtained from materials which had been refined with great care by the zone melting method. The anthracene was excited through a UFS-1 filter and the naphthalene through a UFS-1 and a ZhS-3.

The scintillations were excited by Co^{60} gamma rays and the pulses were oscillographed under the same conditions. Oscillograms of the gamma and photo pulses for anthracene are shown in the Figure (c, d respectively). Their somewhat different shape is explained by the difference of the leading edge which is apparently associated primarily with the duration of the spark. In order to exclude effects of the apparatus function and spark duration, measurements on each trailing edge were begun



Oscillograms of the pulses. a—noise pulses; b—light pulse from the spark; c—gamma-scintillation of the anthracene crystal; d—photoluminescence of the anthracene crystal when excited by the spark.

20 ns (nanoseconds) after the maximum. The decay curve could be followed to the 5-10% level, and in this range closely approximated an exponential. The values obtained for τ are shown in the Table.

Crystal	τ (ns)	
	Photo excitation	Gamma excitation
Anthracene	31 ± 3	29 ± 3
Naphthalene	82 ± 5	86 ± 4

Thus it turns out that the values of τ_f and τ_r are identical within the limits of error of the measurements. It must be pointed out that this conclusion refers only to the interval of the decay that was studied, and does not include either the later or initial stages. In spite of the available data on the exponentiality of the decay law of the radioluminescence of organic crystals over fairly long intervals,[5,6] deviation from exponential behavior is quite possible. In fact, at least in the case of anthracene, the observed duration of luminescence is increased more than three times in comparison to the average lifetime of the excited state of the molecule, because of reabsorption and secondary fluorescence. In the general case, the decay law can be nonexponential[7,8] under these conditions.

The values of τ_r for both crystals agree well with those quoted in other papers. Apparently there are no

data on values of τ_f for naphthalene. The duration of photoluminescence of thick crystals of anthracene, measured by the phase method, is substantially less (14-17 ns, see refs. 2 and 3). In this connection, we measured τ_f for the same anthracene crystal in a fluorometer (modulation frequency 24 Mc). The value obtained also turned out to be less than that measured by the pulse method (15 ns, when measured "by transmission"). Reduction of the amplitude of modulation in this case proved to be stronger than follows from the formula $A_0/A = \sqrt{1 + \omega^2\tau^2}$, which is valid for the exponential decay law. Since, at the modulation frequency indicated, the fluorometer is much more sensitive to the initial portion of the decay than to the latter, it can be assumed that the difference between the values of τ_f determined by the oscillographic and phase methods is explained by the nonexponentiality of the decay due to a large amount of secondary fluorescence.

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THE "SELECTIVITY" OF THE THERMAL EMISSION OF CaO AND MgO

V. A. Sokolov, A. N. Gorban, and N. A. Nazimova (pp. 273-274)

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Many handbooks and monographs on optics point out the marked selectivity of the thermal emission of lime (CaO). Landsberg,[1] for instance, mentions that "the well-known experiment in which pieces of lime and carbon are introduced into a hydrogen flame side by side, and the lime appears to become much hotter than the carbon, is not actually a paradox." The essential cause of this behavior is the fact that the lime, because of the selectivity of its emission in the short wavelength region, compared to a black body (carbon), loses much less energy in the infrared, so that in a given flame it acquires a much higher temperature than carbon does. Other white oxides, including MgO, show similar behavior.[2]

In the present note, we would like to point out another characteristic of white oxides, including CaO and MgO, which has so far escaped attention. In addition to selective emission, this property is doubtless one of the main causes of the above-described "paradox." We have already reported[3] that natural lime has the properties of a crystallophosphor, and may luminesce in a flame as the result of the recombination of free atoms and radicals on its surface, forming molecules. Radical recombination reactions of this type are exothermic; the energy which is released is not only emitted as "cold light," but may also be converted into heat.

At temperatures above the quenching temperature, in the case of luminors, and at any temperature in other cases, the energy of recombination is mainly converted into heat. An object with a high recombination coefficient, placed in a flame, will therefore show a much higher temperature than an object with a low recombination coefficient.

We were able to show this experimentally by the method described in ref. 4: coefficients of recombination were measured in an illuminating gas flame for black copper oxide, magnesium oxide, and lime. The experiment consisted in using a differential thermocouple to measure the difference between the temperatures of two quartz capillaries (outside diam <1 mm). One of the capillaries had a passivated surface (on which atoms and radicals would not recombine); the surface of the other was covered with the oxide under investigation. As in ref. 4, the extreme thinness of the oxide layer practically excludes the possibility of secondary heating of the capillary by the selective emission of the oxide; this was confirmed by heating the capillaries outside the flame (in air, with the aid of an open electric furnace). In the latter case, the temperatures of the two capillaries were identical for all three oxides.

In the illuminating gas flame, the white oxides always showed additional heating due to the energy of recombination. This amounted to ~30° for MgO and ~75° for CaO, corresponding to recombination coefficients of ~0.4 and ~1.0, respectively. The black copper oxide did not show any additional heating.

A simple calculation using Planck's formula shows that for the given temperature difference (at a black body temperature of 1000° K) in the visible range, MgO will emit three times, and CaO ten times more strongly than black copper oxide in the same flame (the free radicals and atoms of the flame being unable to recombine on the surface of the latter).

Thus the unusual brightness of white oxides such as CaO and MgO in chemically active flames (at temperatures above the quenching temperature of luminescence) is due not only to the selectivity of their emission, but to the catalytic behavior of these oxides toward the above-mentioned exothermic reactions as well.

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AN INFRARED ELECTRONIC TRANSITION IN THE Er^{3+} ION

G. S. Krinchik and M. V. Chetkin (pp. 274-275)

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The theoretical scheme of electronic transitions associated with the filling of the f-shell in the rare-earth ions shows that the transitions in the infrared region are caused by spin-orbit splitting of the ground term.[1] Calculation made for the Er^{3+} ion predicts the existence of a $^4I_{15/2}$-$^4I_{13/2}$ transition in the vicinity of 1.5 μ.[1,2] In order to observe this transition, we measured the infrared absorption of the ferrite garnet of erbium $Er_3Fe_5O_{12}$. An IKS-11 spectrograph was used for measuring single crystal platelets of $Er_3Fe_5O_{12}$. The crystals were about 100 μ thick and were cut perpendicular to the [110] axis. A K-30 projection lamp served as the light source, and a PbS photoresistor, cooled to liquid nitrogen temperature, was used as the detector.

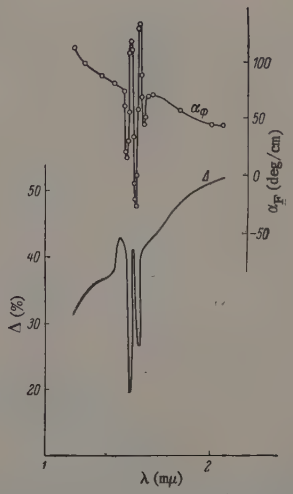
It had previously[3] been shown that in the absorption band region associated with electronic transitions in rare-earth ions, the Faraday effect in ferrite garnet acts like a resonance. Therefore, both the Faraday effect and the absorption were measured in this compound.

The results are shown in the Figure. It is readily seen that for $\lambda \sim 1.5\,\mu$, two absorption lines* around

*In fact, these are not lines, but groups of lines; however, the very fine structure was not resolved in our measurements—the slit width for the absorption measurement was 0.1 mm (~40 cm^{-1}) and for the Faraday effect measurements it was 0.25 mm (~100 cm^{-1}).

6500 and 6600 cm^{-1} are observed in the spectrum; each of these lines corresponds to a resonance curve in the spectrum; each of these lines corresponds to a resonance curve in the Faraday effect. Additional measurements showed that the relative intensities of the observed lines remained essentially unchanged at liquid nitrogen temperatures. This shows that the existence of the two lines does not result from splitting of the ground state $^4I_{15/2}$. The lines also remained when $Er_3Fe_5O_{12}$ was heated above the Curie point and when the absorption of Er_2O_3 was measured.

Wybourne[2] has calculated the energy band scheme of the Er^{3+} ion on the basis of the intermediate bond model. He predicted an energy difference of 6775 cm^{-1} between the $^4I_{15/2}$ and $^4I_{13/2}$ levels. This is comparable with our observed value of 6600 cm^{-1}. The origin of the second absorption line remains unknown. It should be noted that a similar situation is obtained in the identification of the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition, for which two lines around 15300



Transmission coefficient and Faraday effect α_F of an erbium ferrite garnet.

and 15000 cm^{-1} have been observed.[1] Wybourne has hypothesized that the transition of interest was associated with the 15300 cm^{-1} line (the theoretical location was at 15449 cm^{-1}) whereas the 15000 cm^{-1} line was caused by a thulium impurity. In our case, an explanation of the presence of a second line based on impurity effects is excluded, since the intensity of the Faraday effect was approximately the same for both lines. Thus the presence of double lines in the ground term of the Er^{3+} ion is reliably established and requires a theoretical explanation.

We take this opportunity to express our sincere gratitude to G. I. Rukman for helping with this work.

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ON THE DIFFERENTIATION OF SPECTRA

V. A. Zubov (pp. 275-277)

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In a number of recent reports[1,2] the authors, in attempting to narrow the absorption band, have recorded the second or fourth derivative with respect to frequency. The method has been used in qualitative and quantitative analyses. The papers published hitherto have discussed the advantages of the method, the shape of the bands resulting from differentiation, the presence of satellites, and the occurrence of false structure, but have neglected the very important role of random errors, although it is known that differentiation leads to a very appreciable increase in such errors. The rational use of the method necessitates the examination of the role of random errors. Within the context of the problem the spectral approach[3,4] is very convenient.

In order to evaluate the results of differentiation, it is necessary to compare the widths of bands recorded with and without differentiation and also to compare the random errors in the measurement of intensity at the band maximum and in the measurement of the extremum values of the derivative (considering only the even derivatives).

Let us examine the random error (n-th derivative)

$$\sqrt{\overline{\Delta f^{(n)2}}} = \sqrt{\frac{1}{2\pi}\int_{-\infty}^{\infty} \Psi(\omega)\,|G(\omega)|^2\,d\omega}, \qquad (1)$$

where $G(\omega)$ is the Fourier transformation for the differentiation, $\Psi(\omega)$ is the average spectral density of random errors (in terms of intensity), and ω is the argument in the Fourier transform.

At the same time let us examine the width of the contour $f^n(\nu)$ (from here on, "width of the contour" will stand for the half-width of the band in the case of the normal band and for the contour from the zero line to the maximum value in the case of the differentiated bands).

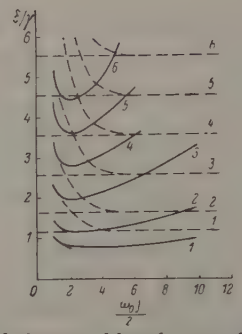
We will make simplifying assumptions which are usual in infrared spectroscopy: (1) the line has a dispersion shape of width J; (2) the slit-function is Gaussian with a width equal to the spectrometer slit-width S; (3) the random errors are independent of the magnitude of the signal and have a uniform spectrum, i.e., $\Psi(\omega) = \Psi_0 = \text{const.}$; (4) exact differentiation can be used in the given case, since then the magnitude of a random error can be infinite [see Eq. (1)].

Let us use the approximate differentiation

$$G(\omega) = \begin{cases} (i\omega)^n, & |\omega| < \omega_0, \\ 0, & |\omega| > \omega_0, \end{cases}$$

where ω_0 is some boundary frequency in the Fourier spectrum. We assume a sharp cutoff of the spectrum on the high frequency side instead of the gradual cutoff which actually occurs due to instrumental inertia.

We have calculated the widths of observed normal bands as a function of ω_0 for different values of the ratio of the slit-function width to the band-width (S/j ranges from 0.5 to 5). We have also calculated the bandwidths



The width of observed bands as a function of ω_0 for different values of the ratio S/j. S is the slit-width for normal operation without differentiation. The full curves represent double differentiation; the dotted curves represent the normal case, without differentiation. The values of S/j: curve 1—0.5; curve 2—1.0; curve 3—2.0; curve 4—3.0; curve 5—4.0; curve 6—5.0.

obtained as a result of double differentiation.* The random errors are smoothed out by widening the slits, and it is assumed at the same time that the errors decrease as the square of the slit-width. The results of the calculations are shown in the Figure.

*We have neglected the deviation of the observed band shape from the dispersion shape. Consideration of this deviation would result in a slight decrease in the bandwidth.

It is clear from the calculated curves that, for a given noise level, differentiation leads to a narrowing of the recorded contour for an appropriate choice of ω_0. The smallest width in the case of differentiation was obtained for $\omega_0 \approx 4/j$ (j is the width of the line investigated); without differentiation, for $\omega_0 \approx 10/j$. Let us cite a few examples. If we operate normally (without differentiation) at $\omega_0 \approx 4/j$, then the improvement in the width of the contour is about twofold for an equal level of random error. If we operate normally (without differentiation) at $\omega_0 \approx 10/j$ (the line is practically unaffected by the high frequency cutoff) then the improvement resulting from going to $\omega_0 \approx 4/j$ and differentiating will be a factor of 1.25-1.5 (depending on the ratio S/j) for the contour width and 1.6 for the random error level.

The results of the foregoing examination apply best to infrared spectroscopy. In the case of Raman spectra, for example, the advantages resulting from differentiation are somewhat smaller. This is due to the dependence of the noise level on the magnitude of the signal.

In conclusion it can be pointed out that the improvement associated with the narrowing of a line by double differentiation is not as great as claimed in some of the foregoing investigations. If the disadvantages of the method are also taken into consideration (presence of

lites, possibility of appearance of false structures, then the wide use of the method can hardly be mmended. In certain specific cases when its use is particularly desirable, it is possible to evaluate the gain obtained thereby from a calculation such as outlined above, using the actual data.

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VECTOR COUPLING IN X-RAY SPECTRA

A. M. Gutman (pp. 277-278)

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The interaction between holes and valence electrons an important role in the hyperfine structure of spectral lines. Both the asymmetry effect[1] and the ing of lines[2] have been explained by this interaction. In examining the interaction between holes and the ce shell, it is impossible to limit oneself to the tional LS- and jj-coupling. The former is not appli- to the x-ray shell (with the exception of an x-ray le), and the latter is mostly applicable to the valence rons. The application of some of the other so-called niform couplings already used in atomic spectra[3-5] t be useful. A general analysis of couplings, including tailed examination of the $l^m l'$ configuration, was e in ref. 6. The analysis of the foregoing configura- is not applicable to the x-ray spectrum, since it was ase of an excited l'-electron that was analyzed in 5.

In the case of an x-ray spectrum with one hole we mmediately limit the coupling by the j' moment of -ray shell. For practical purposes, we may as- e that the electrons are LS-coupled and limit our- s to a single shell.

Let us enumerate the interaction matrices which be diagonalized in achieving vector coupling of the ents L, S, and j', i.e., the interaction matrices ling these moments: F is the nonspherical, multi- part of the direct electrostatic interaction between nner and outer shells, G is the exchange electro- c interaction between these two shells, H_{sl} is the -orbital interaction of the outer electrons.

The most strongly interacting moments are the cipal ones to couple. As was shown in ref. 6, diagon- ation of G is possible only with LS-coupling. Con- ently, satisfactory "purity" of coupling in the x-ray trum with $l' \neq 0$ is possible only if G is small. Let xamine separately the case $l' \neq 0$. For coupling to r, the following conditions must be satisfied: either

$$F \gg H_{sl} + G \tag{1}$$

$$H_{sl} \gg F + G. \tag{1'}$$

The upper inequality leads to the coupling

$$\mathbf{j'} + \mathbf{L_0} = \mathbf{K},$$

hence to

$$\mathbf{K} + \mathbf{S_0} = \mathbf{J}. \tag{2}$$

where L_0 and S_0 are the orbital and spin moments of the valence shell, respectively. This coupling is called jL-coupling. It is symbolized

$$jL_0[K]_{j'}^{2S_0+1}.$$

The moment **K** is the resultant of **s'** not affecting F, and $\mathbf{L_0}$ and **l'** are moments coupled through the F-interaction.

The lower inequality (1') leads to the following scheme:

$$\mathbf{S_0} + \mathbf{L_0} = \mathbf{J_0};\ \mathbf{J_0} + \mathbf{j'} = \mathbf{J}. \tag{2'}$$

This coupling is called Jj-coupling.

jL-coupling is more probable for light atoms and shallow holes, particularly when there is one outer electron and little exchange interaction.[3] Jj-coupling should occur in the case of deep holes and heavy atoms.

For $l' = 0$ the F-interaction disappears due to spherical symmetry. In this case two relations are possible:

$$G \gg H_{sl}, \tag{3}$$

which leads to LS-coupling, and

$$H_{sl} \gg G, \tag{3'}$$

which is the condition for Jj-coupling.

LS-coupling and jL-coupling are more probable in the case of light atoms and shallow holes.

The foregoing considerations obviously hold only for those x-ray spectra in which the nonspherical interaction between the electrons is stronger than the action of the external nonspherical field.

The construction of a wave function for nonuniform couplings can be performed using the methods described in ref. 7.

The author is thankful to I. B. Levinson for critical reading of the manuscript.

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DEPENDENCE OF THE ASSOCIATION OF RHODAMINES ON THE STRUCTURE OF THEIR MOLECULES AND THE NATURE OF THE SOLVENT

L. V. Levshin and I. S. Lonskaya (pp. 278-282)

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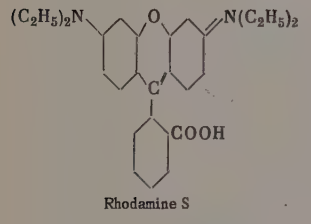
It is well known that, in concentrated solutions, the molecules of many dyes associate with one another. At the same time, the nature of the solvent exerts a substantial influence on the development of association. The aggregates usually form most easily in water, not so well in glycerine, and with great difficulty in alcohols, acetone, and other organic solvents.

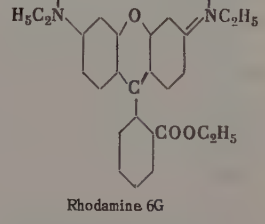
Some authors have endeavored to explain the special position of water in the series of other solvents by the large value of its dielectric constant ($\varepsilon = 81$), which weakens the Coulomb repulsion of dye ions with like charges.[1,2] However, the experiments described in ref. 3, as well as measurements by the authors of the present work, have shown that the magnitude of the dielectric constant of the solvent does not exert a decisive influence on the development of association of the dye molecules.

Along with this, the suggestion has been expressed in refs. 4 and 5 that the principal cause of the appearance of associated molecules in dye solutions consists in the formation of hydrogen bonds among them. In this case, the determining factor in the formation of aggregates must be the presence within the molecules of a possibility of forming hydrogen bonds, either directly with one another or with the help of solvent molecules which serve as intermediate links between the associating dye molecules. The purpose of the present work consisted in a test of these ideas.

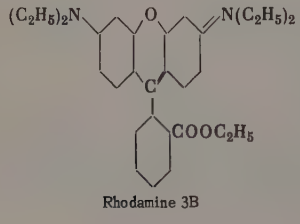
The association processes were studied among molecules of three related dyes—rhodamine S, rhodamine 6G, and rhodamine 3B, the structural formulas of which are presented below.



Rhodamine S



Rhodamine 6G



Rhodamine 3B

These dyes are very suitable by reason of the fact that they are extensively associated in aqueous solvents and, despite the similarity of their structural formulas, they have different possibilities for the formation of hydrogen bonds with one another. Thus rhodamine S has an active OH group, which is lacking in rhodamines 6G and 3B, while rhodamine 6G possesses two polar N—H bonds which do not exist in rhodamines S and 3B. These differences enable us to suppose, in case the effect of hydrogen bonds is decisive, that the association of each of these substances will develop differently in different solvents.

The association of the rhodamines in water has been thoroughly studied in refs. 4-6, where it was shown that at identical solution concentrations, the degree of association (1 – X, where X is the fraction of monomers in the solution) diminishes in going from rhodamine 6G to rhodamine S and then to rhodamine 3B. The value of the binding energy of the associated molecules of these substances is also not the same; it amounts to ~10 kcal/mole in rhodamine S, ~7 kcal/mole in rhodamine 6G, and ~5 kcal/mole in rhodamine 3B.

The rhodamines also associate in glycerine solutions where their presence manifests itself at far greater concentrations than in water. In glycerine solutions also, rhodamine 6G molecules show the greatest tendency to association and rhodamine 3B molecules the least.

In alcoholic solutions, association of the rhodamines is found in still more concentrated solutions. Thus, in an alcoholic solution of rhodamine 3B at $C = 8 \times 10^{-2}$ gm/ml, less than 5% of the molecules are in the associated state.[8] The molecules of the rhodamines behave in a similar way in chloroform ($\varepsilon = 5$) and in formamide ($\varepsilon = 109$).

The behavior of molecules of the rhodamines in binary solvents is very interesting. It was shown in ref. 7 that rhodamine 6G molecules are highly associated in a mixture of dioxane (95%) and methyl alcohol (5%).* The experiments have been repeated by us over a still wider range of dye concentrations (Fig. 1). Values of the degree of association of the solutions under study were computed from the absorption spectra obtained. The results of these calculations are presented in the Table.

*The dyes do not dissolve in pure dioxane.

C (gm/ml)	$1 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$3 \cdot$
Dioxane (95%) + methyl alcohol (5%); 1 – X	0.00	—	0.08	0.10	0.14	0.22	0.47	0.57	
Dioxane (95%) + chloroform (5%); 1 – X	0.00	0.05	0.17	0.26	0.36	0.69	0.78	—	

The temperature dependence of the absorption spec- of concentrated solutions in these mixtures having n studied by means of the method described in ref. 5, as possible to determine the magnitude of the bond- energy U of associated molecules of rhodamine 6G. corresponding dependence of $\log\{[X^2/(1-X)]C\sqrt{T}\}$ /T for $C = 5 \times 10^{-4}$ gm/ml is presented in Fig. 2. tangent of the angle made by this line with the hori- al axis is $\tan\varphi = -(U/k)\log e$, whence $U = 5.5 \pm 0.5$ /mole.

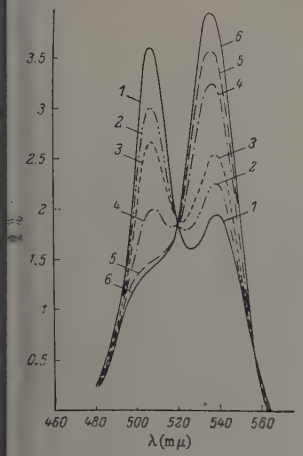


Fig. 1

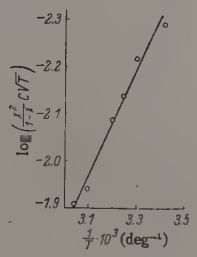


Fig. 2

Fig. 1. Concentration dependence of the absorption spectra of solutions of rhodamine 6G in a mixture of dioxane (95%) with methyl alcohol (5%). Concentration (gm/ml): curve $1-3 \times 10^{-3}$; curve $2-1 \times 10^{-3}$; curve $3-5 \times 10^{-4}$; curve $4-1 \times 10^{-4}$; curve $5-1 \times 10^{-5}$; curve $6-1 \times 10^{-6}$.

Fig. 2. Dependence of $\log\{[X^2/(1-X)]C\sqrt{T}\}$ on 1/T for rhodamine 6G in a mixture of dioxane (95%) with methyl alcohol (5%) ($C = 5 \times 10^{-4}$ gm/ml).

We found a still stronger concentration effect with tions of rhodamine 6G in a mixture of dioxane (95%) chloroform (5%), in which association is even more nsively developed than in water (Fig. 3). The values e degrees of association of these solutions are pre- ed in the Table. It should be noted that the degree ssociation of rhodamine 6G molecules falls off dly with an increase in the concentration of methyl nol or chloroform in such a mixture.

At the same time, association of molecules of rho- ines S and 3B in the same dioxane-methyl alcohol dioxane-chloroform mixtures is practically absent C ~ 5×10^{-3} gm/ml. As an example, two absorp- spectra of rhodamine S at different solution con- rations in a mixture of dioxane and methyl alcohol presented in Fig. 4. These spectra practically co- le.

It can be seen from the data presented that associa- of dye molecules may be extensively developed not in water, but also in other media, apart from its ndence on the magnitude of their dielectric constant. refutes the assertion of certain authors concern- he exclusive position which water occupies in the es of other solvents when association processes and henomena of concentration quenching of lumines- e are considered.[1] At the same time, the regulari-

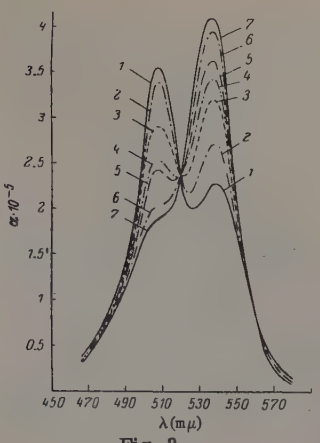


Fig. 3

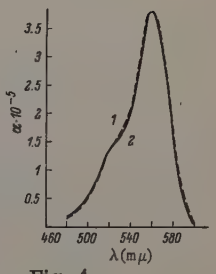


Fig. 4

Fig. 3. Concentration dependence of the absorption spectrum of solutions of rhodamine 6G in a mixture of dioxane (95%) with chloroform (5%). Concentration (gm/ml): curve $1-5 \times 10^{-4}$; curve $2-1 \times 10^{-4}$; curve $3-5 \times 10^{-5}$; curve $4-2 \times 10^{-5}$; curve $5-1 \times 10^{-5}$; curve $6-5 \times 10^{-6}$; curve $7-1 \times 10^{-6}$.

Fig. 4. Absorption spectra of solutions of rhodamine S in a mixture of dioxane (95%) with methyl alcohol (5%). Concentration (gm/ml): curve $1-1 \times 10^{-3}$; curve $2-1 \times 10^{-5}$.

ties which have been noted may be explained by the formation of hydrogen bonds between molecules in the solution.

From the structural formula of rhodamine 3B, one can see that its molecules cannot form hydrogen bonds directly with one another. However, such a bond may be established with the help of a water molecule which unites the dye molecules through oxygen or nitrogen atoms. Since the bonding energy of aggregates of rhodamine 3B is ~5 kcal/mole,[4] it appears that in this case only a single hydrogen bond is formed.

In rhodamine 6G molecules, there are hydrogen atoms in half-substituted amino groups, and this permits us to assume the possibility of the formation of hydrogen bonds directly between dye molecules.

The bonding energy of aggregates of rhodamine S is ~10 kcal/mole.[6] In this case, there apparently exists a double hydrogen bond, which, however, can be established in different ways: either directly between rhodamine S molecules through the COOH groups, or, with the help of water molecules, through the nitrogen and oxygen atoms of the dye molecules.

Glycerine molecules also contain two OH groups [sic] and therefore the same possibilities exist in this case as in water. However, as experiment shows, such bonds have a far lower probability of forming in glycerine.

The low degree of association of the rhodamines in alcoholic solutions is apparently brought about by the fact that the alcohol molecules form hydrogen bonds, through their OH group, with the oxygen and nitrogen atoms of the dye molecules, preventing their direct association through these atoms. At the same time, by virtue of their structure, the alcohol molecules cannot, like water molecules, unite two rhodamine molecules into a dimer.

The insignificant association of the rhodamines in chloroform solutions (Cl_3C-H) may be brought about by

the formation of a hydrogen bond between the C—H groups of the solvent molecules and the dye molecules. Such a bond can be realized in the case of chloroform.[8]

In formamide ($HCONH_2$), association of the rhodamines is extremely weak. According to our data, not more than 2-3% of the molecules are in the associated state at $C \sim 1 \times 10^{-2}$ gm/ml. This, apparently, is also brought about by the fact that the formamide molecules form hydrogen bonds with the dye molecules, preventing their association with one another. It follows from the data presented above that the character of the association of rhodamine 6G molecules is roughly the same in dioxane-methyl alcohol mixtures and in dioxane-chloroform mixtures. Apparently, dimers of rhodamine 6G molecules are formed in solution in both cases, being joined together either directly through NH groups or with the help of dioxane molecules which form hydrogen bonds with their NH groups. The methyl alcohol and chloroform which are present in the mixture to the extent of 5% may somewhat reduce the degree of association in the solution, forming hydrogen bonds with a certain part of the dye molecules.

It is not difficult to understand why rhodamine 3B molecules do not form aggregates in binary mixtures. The OH and NH groups are lacking in them, and consequently dioxane molecules cannot promote their association. Together with this, as was already noted above, hydrogen bonds directly between rhodamine 3B molecules can not arise either.

The absence of aggregates of rhodamine S in binary mixtures of dioxane with methyl alcohol and dioxane with chloroform indicates that, in such media, no hydrogen bond forms directly between the molecules of this dye.

In conclusion, the authors offer their sincere thanks to L. A. Ignat'eva for helpful discussion of the results of the present work.

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THE KRISHNAN EFFECT

D. K. Beridze and M. I. Shakhparonov (pp. 282-284)

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Suppose that a beam of light with its electric vector along the Y-axis is propagated in a liquid along the X-axis. Let us consider the degree of depolarization of the light scattered once through 90°, that is, along the Y-axis. It is well known that:

$$\Delta_h = \frac{(I_X)_h}{(I_Z)_h},$$

where $(I_X)_h$ and $(I_Z)_h$ are components of the intensity of the scattered beam along the X and Z-axes. According to Rayleigh's equation:

$$(I_Z)_h = (I_X)_V. \quad (1)$$

In addition, for light scattered once through 90°:

$$(I_X)_h = (I_X)_V, \quad (2)$$

where $(I_X)_V$ is the component of the intensity of the scattered light for the case where the electric vector of the incident light is along the Z-axis.

Equations (1) and (2) have a more general meaning. It follows from them that $\Delta_h = 1$.

In 1935, however, Krishnan[1] observed that in the region of critical opalescence, $\Delta_h > 1$. The measurements reported in ref. 1 were made by visual photometry; the angle of observation was not reported. According to Krishnan, as $\Delta T = T - T_{cr} \to 0$, $\Delta_h \to 4$ (for a mixture of 85% CS_2 + 15% CH_3OH with a critical temperature of about 40°C). Krishnan observed a deviation of Δ_h from 1 even at temperatures of 60°C. This is known in the literature as the Krishnan effect.[2] Krishnan[1] and Gans[3] are of the opinion that the deviation of Δ_h from unity is caused by fluctuations comparable in size to the wavelength λ. However, Krishnan observed a considerable deviation of Δ_h from unity even at $\Delta T \sim 10°C$, when the light scattering follows Rayleigh's law perfectly well, and consequently the mean amplitude of the fluctuations is much less than λ. The Krishnan effect was subsequently detected and studied in the neighborhood of the critical liquid/vapor point, as well as in glasses and polymers.

We have measured Δ_h for light scattered by the systems nitrobenzene-n-hexane, nitrobenzene-n-heptane and methyl alcohol-cyclohexane at concentrations corresponding to the critical solution point.

The method is described in ref. 4. The diameter of the incident light beam was 2 mm. The photometer made it possible to observe the scattering volume at a vertical angle of $\varphi_V = 2°$ and a horizontal angle of $\varphi_H \sim 10'$; the vertical angle could be reduced to 30'. The scattering coefficient in the nitrobenzene-hexane and nitrobenzene-heptane mixtures followed the Rayleigh law down to ΔT 0.1°C. In agreement with Chow Quantil,[5] deviations from the Rayleigh law are observed at $\Delta T \leq 1.0°C$ for methyl alcohol-cyclohexane solutions. Our measurements show that Δ_h differs considerably from unity when ΔT is between 0 and 2°C, but the difference was considerably smaller than that found by Krishnan. The difference Δ_h 1 depends strongly on the dimensions and shape of the cell and the scattering volume. The cell was formed of

ass tube 0.8 cm in diameter, with plane windows
d to the ends. With immersion the value of Δ_h for
t scattered by the nitrobenzene-heptane solution
ged from 1.037 at $\Delta T = 0.350°C$ to 1.55 at $\Delta T =$
5°C. Close to the front window of the cell, the pri-
y scattering was relatively high and Δ_h relatively
As the distance l from the first window to the cen-
of the scattering volume increased, both the diffuse
ttering and Δ_h gradually increased. At $l \geqslant 10$ mm,
light scattering in this temperature interval ΔT ap-
ently becomes completely diffuse and Δ_h becomes
stant. As the angle of observation φ_V of the photo-
er along the Z-axis decreases, Δ_h decreases. The
le shows some of the changes in Δ_h observed in the
described above at 5780 A.

ΔT (°C)	l (mm)	φ_v deg	Δ_h	ΔT (°C)	l (mm)	φ_v deg	Δ_h
0.340	5	2.5	1.04	0.125	5	1.0	1.21
0.340	10	2.5	1.14	0.125	10	1.0	1.29
0.340	22.5	2.5	1.13	0.125	5	1.5	1.34
0.150	5	2.0	1.15	0.025	5	0.5	1.55
0.150	10	2.0	1.24	—	-	—	—

The experimental results lead to the conclusion that
Krishnan effect is probably associated with the con-
ons of observation of the scattered light in the pres-
of multiple scattering, and not with the properties
ne individual scattering particles or fluctuations. In
with multiple scattering Eq. (2) is no longer valid,
e the light may be propagated along the Y-axis after
tering through angles different from 90°.
Our measurements of the extinction coefficient τ of
nitrobenzene-heptane mixture at the critical concen-
tration showed that $\tau \approx 0.25\ cm^{-1}$ at $\Delta T = 0.350°C$ and $\tau \approx 0.8\ cm^{-1}$ at $\Delta T = 0.165°C$; from this, by extrapolation, we obtain $\tau \approx 5\ cm^{-1}$ at $\Delta T = 0.025°C$. The mean number of scattering collisions $\bar{Z}$ suffered by a light quantum in a medium of optical thickness $a = \tau l$ can be estimated approximately by using the equation[6]:

$$\bar{Z} = \frac{24(1+a) + 8a^2 + a^3}{12(2+a)}. \qquad (3)$$

If we use the cell radius for the geometrical thickness of the scattering layer ($l = 0.4$ cm), we obtain $\bar{Z} = 1.008$ for $\Delta T = 0.350°C$, $\bar{Z} = 1.17$ for $\Delta T = 0.165°C$, and $\bar{Z} \approx 2.5$ for $\Delta T = 0.025°C$.

To account theoretically for the observed deviations of Δ_h from unity, the radiative transfer equation with allowance for polarization effects must be solved for the case in point.

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THE FREE ELECTRON MODEL APPLIED TO THE THIOPHENE MOLECULE

T. N. Rekasheva (pp. 284-286)

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The thiophene molecule C_4H_4S belongs to the class of cyclic diene hydrocarbons, that is, it forms a plane pentagonal ring with two unsaturated bonds located symmetrically with respect to the YZ plane (Fig. 1a). These closed systems cannot be called conjugated in the sense understood by chemists. Nonetheless, the great similarity between the properties of thiophene and benzene has led chemists to suppose that the well known free circulation in a closed path occurs in this case also for the π-electrons of the double bond and the p-electrons of the sulfur atom.*

*Mulliken[1] calls this type of conjugation in thiophene and some other cyclic dienes "heterocyclic conjugation."

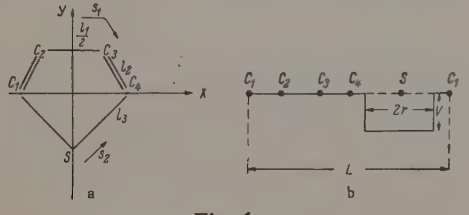

Fig. 1

On this basis, we have assumed that six mobile electrons can move around the perimeter of the ring in the thiophene molecule—four π-electrons (one from each carbon atom) and the two p-electrons belonging to the sulfur atom. To allow for the inductive effect of the electronegative sulfur atom on the potential profile, a depression V is introduced at the location of this atom. This depression is evaluated from the equation:

$$V = \frac{I_S^I + I_S^{II} + A_S}{3} - \frac{1}{2}(I_C + A_C),$$

where I_S^I and I_S^{II} are the first and second ionization potentials of the sulfur atom, A_S is the electron affinity of the sulfur atom, and I_C and A_C are, respectively, the ionization potential and electron affinity of the carbon atom. A value of 0.215 a.u. was found for V.

Figure 1b shows the shape of the floor of the potential well in which the mobile electrons of the molecule move. The quantities l_1, l_2, l_3, the length of the potential well L, and the width of the depression 2r are determined from the known lengths of the C—C, C=C, and C—S bonds in the thiophene molecule and the covalent radius of the sulfur atom. These quantities are taken to be (in a.u.): $l_1 = 2.73$, $l_2 = 2.56$, $l_3 = 3.30$, $2r = 3.80$, $L = l_1 + 2l_2 + 2l_3 = 14.45$.

The linear coordinates expressing the distance along the bond (as shown in Fig. 1a) are designated S_1 and S_2 and lie within the following limits:

$$-a \leqslant s_1 \leqslant a, \qquad -r \leqslant s_2 \leqslant r,$$

where $a = (l_1/2) + l_2 + l_3 - r$.

The wave functions of the stationary states were determined individually for parts I and II of the molecule. The following expressions were obtained for the symmetric ψ_{is} and the antisymmetric ψ_{ja} wave functions:

$$\psi_{is} = \begin{cases} A_i \cos \alpha_i s_1, & -a \leqslant s_1 \leqslant a, \\ A_i \dfrac{\cos \alpha_i a}{\cos \beta_i r} \cos \beta_i s_2, & -r \leqslant s_2 \leqslant r, \end{cases}$$

$$\psi_{ja} = \begin{cases} A_j \sin \alpha_j s_1, & -a \leqslant s_1 \leqslant a, \\ A_j \dfrac{\sin \alpha_j a}{\sin \beta_j r} \sin \beta_j s_2, & -r \leqslant s_2 \leqslant r, \end{cases}$$

where A_i and A_j are factors determined from the normalizing conditions, $\alpha_i = \sqrt{2E_i}$, $\beta_i = \sqrt{2(E_i + V)}$, $\alpha_j = \sqrt{2E_j}$ and $\beta_j = \sqrt{2(E_j + V)}$. The energy levels of the symmetric and antisymmetric states are represented by E_i and E_j respectively.

By solving the secular equation for the symmetric and antisymmetric wave functions we obtain the energy level diagram of the π-electrons in the molecule, as shown in the Table (in a.u.) together with the appropriate symmetry states.

E_1 (c)	−0.119
E_2 (c)	0.048
E_3 (a)	0.064
E_4 (a)	0.315

Thus, for a transition with the lowest frequency $E_3 \rightarrow E_4$, the energy difference $E_4 - E_3 = 0.251$ a.u. and the frequency $\nu_{3\rightarrow4} = 55{,}000\ cm^{-1}$ are obtained. Comparison with the corresponding experimental value $\nu = 42{,}000\ cm^{-1}$ [1] gives a discrepancy of the order of 30%, which is typical for this type of computation.

The wave functions found were used to calculate the oscillator strength for the transition under discussion (polarized parallel to the OX axis). The following value was found:

$$f = 0.24.$$

This value may be compared with the corresponding experimental value $f = 0.05$.[1] The large discrepancy is not surprising. It is well known that many calculations of oscillator strengths based on other quantum-mechanical methods lead to f values which are considerably higher than the experimental values. For example, Mulliken,[2] using the LCAO method, obtained $f = 0.33$ for the longest wavelength transition in the cyclopentadiene molecule. The data of various workers give an experimental value of 0.04 to 0.05.

We used the wave function we obtained to find the distribution of electron charge density along the half-perimeter of the thiophene ring corresponding to the individual stationary states, and we also calculated the resultant charges of the atoms forming the thiophene molecule (Fig. 2). The distribution obtained showed that the

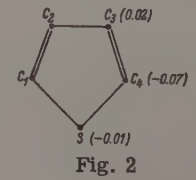

Fig. 2

ron cloud of the ground state is concentrated near ulfur atom. In other words, this distribution was as o electrons of the sulfur molecule essentially did not part in the movement along the molecule as a whole; is, only the four π-electrons of the double bond were lly mobile. This conclusion seems completely logi- rom a physical point of view.

The calculated values of the charges on the atoms e with experimental chemical data on substitution re- ns involving the action of electrophilic reagents on hene. As is well known, halogens, nitro-groups and o-groups enter the thiophene molecule in the α- ion (C_1 or C_4 atoms) and not in the β-position (C_2 atoms).

Kikuchi[3] also calculated the thiophene molecule by CAO method, using the idea of hybridization of the d orbits of the sulfur atom suggested by Longuet- ns[4] for thiophene. The parameters entering the omb and resonance integrals were chosen so as to give agreement between the observed and calculated values of the bond energies and the dipole moments of the thiophene molecule. The frequency thus found for the longest wavelength absorption line agrees with experiment. The electron charge densities in the α and β positions are 1.0249 and 1.0174 respectively.

In conclusion, I wish to thank Professor M. G. Veselov for his advice and constant encouragement.

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NEW DATA ON THE ABSORPTION SPECTRA OF THIAZINE DYE CRYSTALS

N. M. Melankholin (pp. 286-289)

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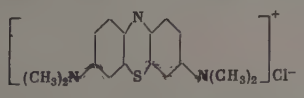
n 1957, we published[1] the absorption spectra of als of three thiazine dyes.* The spectra were ob-

added in proof: It has just been established that bsorption maximum at 550 mμ is intrinsic to liquid als of methylene blue.

d with a photoelectric microspectrophotometer con- ted by us[2] and provided with an FEU-19 photomulti- , and were recorded to 630-640 mμ on the long-wave- h side. Later, after the apparatus had been provided a second photomultiplier (an FEU-22), the absorp- spectra of other thiazine dyes, measured out to 00 mμ, were published.[3,4] This enabled us to re- all the electronic bands located within the limits of isible and near infrared regions of the spectrum. n this connection, the need arose to obtain the ab- ion spectra, in the same region, of the three thia- dyes previously investigated: methylene blue, ylene green, and novomethylene blue. Their absorp- curves for vibrations parallel (or approximately llel) to the principal axes of the indicatrix were re- ured by us out to 860 mμ. The marked fall in ab- ion intensity in the infrared region of the spectrum he low value of the absorption in the region begin- at 800-860 mμ show that longer-wavelength elec- c bands are apparently lacking in the absorption ra of the crystals investigated.

The absorption spectra of crystals of methylene



measured at the same sections of the indicatrix as e, and all the absorption bands found in ref. 1 may en in them. The newly obtained curves allow us to mine more precisely the position of the most in- absorption band, which corresponds to vibrations llel to N_g (Fig. 1); its maximum is located at 560 mμ.

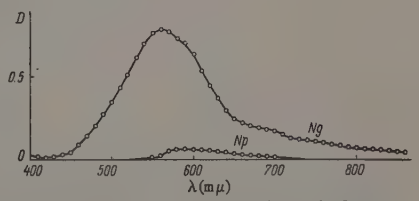
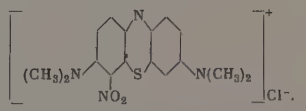


Fig. 1. Absorption spectra of methylene blue crystals in a section parallel to the N_gN_p plane.

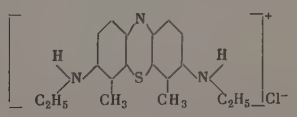
The weak shoulder on the same absorption curve indicates the presence of one more very weak absorption band around 700 mμ.

Analogous experiments were carried out on crystals of methylene green.



The newly obtained absorption spectra contain, aside from the previously established bands, a clearly-marked band at 680 mμ (Fig. 2a). Since this band is noticeable on the curves corresponding to differently oriented vibrations, one may draw the conclusion that it is weakly polarized. Furthermore, for vibrations parallel to N_g, one more intense absorption band was discovered around 730 mμ (Fig. 2b); it was not noticeable on the absorption curves of samples oriented in other ways—i.e., it is highly polarized.

For crystals of novomethylene blue,



the absorption spectra were remeasured at two sections

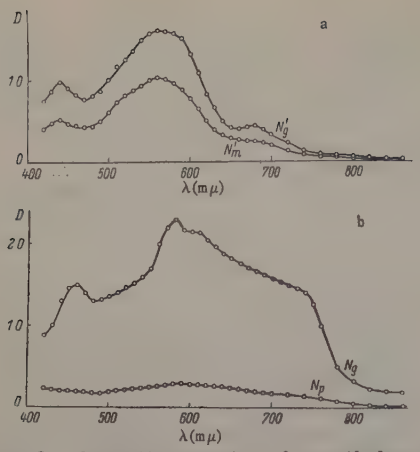


Fig. 2. Absorption spectra of a methylene green crystal in an oblique section (a) and in a section parallel to the N_gN_p plane (b).

of the indicatrix, parallel to the N_gN_m and N_mN_p planes. These spectra first of all confirm that the fundamental absorption band which was approximately established earlier for vibrations along N_g is actually located around 640 mμ (Fig. 3). For the same vibrations, a weak but clearly-marked absorption band at 410 mμ was found. Furthermore, a weak shoulder on the absorption curve for these vibrations indicates the presence of one more fairly intense absorption band around 720 mμ. No new bands were found in the remaining absorption curves of the novomethylene blue crystal.

Thus the absorption curves newly obtained over a broader spectral region for crystals of methylene blue, methylene green, and novomethylene blue have enabled us to find, in the spectra of these crystals, new absorption bands lying in the red and near infrared regions of the spectrum. The new data augment the experimental data previously obtained for the dyes listed. The presence of a long-wavelength absorption band located around 700-730 mμ is a common peculiarity of the crystal spectra of all three dyes studied. This band is fairly pronounced in methylene green and novomethylene blue, but

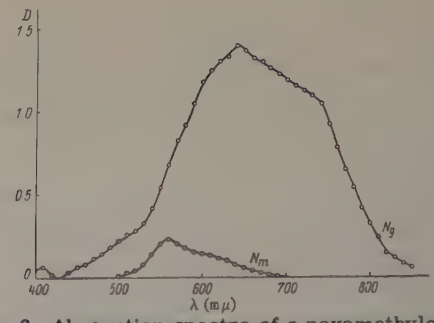


Fig. 3. Absorption spectra of a novomethylene blue crystal in a section parallel to the N_gN_p plane.

is hardly noticeable in methylene blue. Since it is the longest-wavelength absorption band of these crystals, it should apparently be considered as a purely crystal band; i.e., as one produced by intermolecular bonds in the crystal lattice.* The similarity in the positions of this band in the crystal spectra of all three dyes indicates in this case the similarity of the structures of the crystals referred to.

*This assumption is based on the fact that, in crystals of methylene blue, for which the position of the molecules in the lattice has been established, the band with the longest wavelength of the three fundamental absorption bands is a purely crystal one, since it corresponds to vibrations perpendicular to the plane of the molecule.

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THE EFFECT OF NITROGEN ON EXCITED MERCURY ATOMS

I. Agyrbichanu, I. Kukurezyanu, V. Vasiliu, and I. Popesku (pp. 289-290)

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The effect of nitrogen on the 6^3P_1 mercury level has attracted attention. In his doctoral thesis,[1] Kastler scribes both his own results and those of other investigators. However, it was not until 1955 that Berberet and Clark[2] made a quantitative study of the change in population of the 6^3P_0 level following collisions of the second kind between N_2 molecules and mercury atoms in the 6^3P_1 state.

They determined the attenuation of Hg I 4047 A in passing through a cell containing excited Hg atoms and nitrogen as a function of nitrogen pressure.

No quantitative measurements have been made of the variation of the intensity of the components of the fluorescent HgI triplet ($7^3S_1 \rightarrow 6^3P_{0,1,2}$) with nitrogen pressure. This triplet is excited according to the scheme:

$$6^1S_0 \xrightarrow{2537\ \text{Å}} 6^3P_1 \xrightarrow{N_2} 6^3P_0 \xrightarrow{4047\ \text{Å}} 7^3S_1,$$

However, research on the effect of nitrogen on the 7^3S_1 triplet level has led to somewhat contradictory results. For example, Richter[3] measured the polarization of the components of this triplet and found that nitrogen does not affect the Hg atoms which are in the 7^3S_1 state, while Kastler[1] reached the opposite conclusion from similar experiments. Nonetheless, a quantitative knowledge of the dependence of the intensity and degree of polarization of components of the fluorescent triplet on nitrogen pressure is important in studies of the optical and magnetic resonance of these levels.

We have used a dual optical and magnetic resonance apparatus of our own construction, with photoelectric detection, to determine the dependence of the intensity I and degree of polarization P of the components of the lines 5461, 4358, and 4047 A on nitrogen pressure. Figure 1 is a diagram of the apparatus used.

The method described in ref. 2 was used to obtain chemically pure nitrogen. The Table and Fig. 2 show the experimental results.

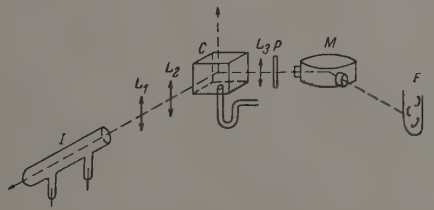

Fig. 1. Diagram of the apparatus. I—light source; L_1, L_2, L_3—lenses; C—cell containing the fluorescent material; P—polarizer; M—monochromator; F—FEU-17 photomultiplier.

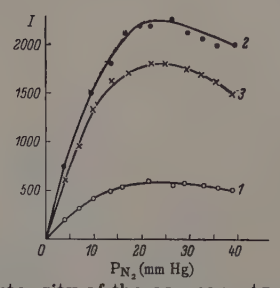

Fig. 2. Intensity of the components of the fluorescent triplet Hg I plotted against nitrogen pressure. Wavelengths: curve 1—4047 A; curve 2—4358 A; curve 3—5461 A.

The data show the existence of an optimum nitrogen pressure (25 mm Hg) for all three components of the triplet. We note that Berberet and Clark[2] found that the maximum absorption of the 4047 A line, and hence the maximum population of the metastable 6^3P_0 level, occurs at about 25 mm Hg.

λ = 4047 Å	P_{N_2}	4.5	7.5	11	14	18	23	26	28	32	—	—
	(mm Hg) P (%)	68	69	67	67	63	63	62	64	66	—	—
λ = 4358 Å	P_{N_2}	3	4.5	7	10	14	16.5	20	23	26	29	32
	(mm Hg) P (%)	25	27	27	28	28	29	29	29	28	30	30
λ = 5461 Å	P_{N_2}	1	3	4.5	7.5	10	13	18	22	25	29	32
	(mm Hg) P (%)	10	9	10	8	9	10	10	10	8	9	9

Note: The ratio of the signals from fluorescent and scattered light ≥ 10; the ratio of the signals from fluorescence and dark current ≥ 50. For λ = 4047 and 4358 A, measurements were not made at pressures below 4.5 and 3 mm Hg, respectively, owing to the low accuracy resulting from the low values of the fluorescence/scattered light ratios (less than 2).

Our data also indicate that in this pressure range, effective saturation is reached for the stepwise excitation of the fluorescent triplet. The constant value of the degree of polarization with changing nitrogen pressure (see the Table) shows that the pressure of nitrogen scarcely affects the 7^3S_1 level.

A more complete account of the experiment will be published later.

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EMISSION ANALYSIS OF ATOMIC MATERIALS. BY A. N. ZAIDEL', N. I. KALITEEVSKII, L. V. LIPIS, AND M. P. CHAIKA. PROF. A. N. ZAIDEL', EDITOR.

Fizmatgiz (State Publishing House for Physics and Mathematics), Leningrad-Moscow, 1960, 686 pp.

(pp. 291-293)

The book under review is a systematic presentation of the work done by the authors in the field of spectral analysis of pure and super-pure materials. Interest in such work is very great at present; the modern techniques of atomic and semiconducting materials require the solution of analytical problems of detection of impurities in extremely low concentrations, working often with a very limited sample. The authors are recognized experts in this difficult branch of spectral analysis, and one should acknowledge their effort in the preparation of this book. Other work than the authors' is also represented in the book, thus making it a formidable monograph, which is much needed and which will undoubtedly be welcomed by specialists in spectral analysis. It will make a good manual for their work.

The book consists of three parts: The first part is an auxiliary one. It contains some general problems of spectral instrumentation, and also new material which has not yet received attention in our literature, on spectral analysis, for instance, diffraction instruments, and the Fabry-Perot etalon. The problem of sensitivity of spectral analysis is presented in an interesting manner, based on considerations of the signal to noise ratio (i.e., the intensity of a spectral line relative to that of the continuous spectral background). Attention is given to the question of the accuracy of the analysis. The various types of spectral apparatus are considered by comparing their basic characteristics: the resolving power and, especially, the light speed. It is shown, in particular, that instruments with modern diffraction gratings are not inferior to prism apparatus with respect to light speed. Various light sources for spectral analysis are discussed, including discharge tubes and tubes with a hollow cathode.

The material of the first part is presented in an original and interesting manner, and is linked with the main idea of the monograph—the determination of small concentrations with small samples. Unfortunately, in this part, poor definitions and conclusions and annoying misprints may be found. Some examples follow.

On page 21 there is a sentence: "...therefore the amount of exposure It (where t is the time of exposure) as well as the galvanometer readings in the photoelectric measurements, are called the intensity" (italics are mine—V.P.). First of all, the quantity It is called the amount of illumination, and it is not identified as the intensity; nor are the galvanometer readings. This terminology is not the "usual" one, as the authors say, and it should be carefully avoided, because it leads to confusion and false conclusions. If we set the ratio of galvanometer deviations in photoelectric measurements of light fluxes equal to the intensity ratio, it does not mean that we identify them. In a book like that under review, one should give rigorous definitions.

The expression (4) on page 26 should be called Lom kin's formula, or, at least, the Lomakin-Scheibe formul

There is a misprint in Eq. (6); it should be $\gamma \log a$, instead of $\log a$.

"Visual interpolation of blackenings in a spectrum taken through a step-filter" (I quote from p. 31) is calle in our practice "photometric interpolation"; there is no reason to replace this term by another one.

Considering the dependence of the intensity of spec tral lines on concentration in the sample, one has to introduce explicitly a quantity which characterizes the los of the material of the sample into the gaseous phase. This quantity cannot be considered independent of the composition of the sample in all cases.

It is questionable whether it is necessary to give th very rough and poorly justified estimation of the sensitivity of the determination of an element on the basis of the number of possible lines (p. 57).

In Eq. (4), p. 111, it should be 10^2, instead of 10^3.

In Eq. (8), p. 112, a quantity S/f_2^2 appears which characterizes the light speed of the spectrograph, where S is the area of the actual aperture and f_2 is the focal length of the camera lens. This quantity cannot always be considered close to the square of the relative aperture of the camera lens, because the difference between these two quantities is such, particularly at the spectru edges, that their ratio may amount to several units. It is sufficient to examine the high speed cameras of the spectrograph ISP-51, to convince oneself on this point. It is more correct to call this quantity the relative aperture with respect to the spectrograph camera.

A quartz prism (p. 125) is manufactured in such a manner that the light rays travel in it along the optic axis of the crystal (for minimum deviation); in this case there is no double refraction: there is only a rotation o the plane of polarization, which results in this case in doubling of spectral lines. In a Cornu prism, it is precisely this rotation of the plane of polarization that is compensated. Therefore Fig. 32 is misleading; it may appear from the figure that the directions of the optic axis in the two halves of the prism are mutually perpen dicular, which is not true.

In the equation for the diffraction grating (36), p. 1 it is necessary to give the sign rule for the angles of in cidence and diffraction.

In Eq. (44) and in its interpretation following on p. 128, the symbols I and I' are interchanged. It is incorrectly pointed out that for $Nv = k_2\pi$, maxima are observed when $v = k_1\pi$. This is true only when $k_2 = k_1N$ for all other values of k_2 minima are observed. The magnitude of the main maxima decreases not inversely proportional to the square of the spectrum order, as stated on p. 128, but according to the change of the factor in Eq. (44) which corresponds to the diffraction in a

e opening (groove) of the grating.
Eq. (19) is derived for a system which has a focusing
s separate from the diffraction device. This equa-
annot be used for an apparatus with a concave dif-
on grating, because the linear magnification in in-
nents of this kind is determined differently. Such
ification takes place only along the slit image,
eas in the direction of dispersion perpendicular to
ay, the width of the slit image is equal to the width of
ntrance slit. When the length of the entrance slit is
iently large so as to produce full illumination in the
e of the line, then the light speed of the spectrograph
ermined by $L = \tau S/\rho^2$, where ρ is the radius of
ture of the grating (p. 136).
or the light speed of spectrometers with a prism
grating, Eq. (73), p. 145, that is,

$$\gamma = \frac{dn}{d\lambda} \cdot \frac{\lambda}{2 \sin \psi},$$

ained. Here the first factor refers to the prism
n, the second to the system with the diffraction
g in an autocollimative arrangement. Next, a spec-
se $\varphi = 30°$ is considered, and the formula becomes
$dn/d\lambda$). A graphical analysis of the change of the
ity γ for different values of λ is made for various
rsing materials. This kind of handling of Eq. (73)
permissible: λ and φ are connected with each
in this case by the grating condition $k\lambda = 2d \sin\varphi$,
ey cannot be independently changed. By selecting
icular value for the diffraction angle φ, we are
y restricted as to the value of the wavelength.
a consideration of this restriction, we see that
3) must be written: $\gamma = (d/k)(dn/d\lambda)$.
the description of generators with electronic
l (p. 209), the scheme of the generator GEU-1
by us should be given.
is pointed out on p. 214 that in a spark the dura-
f the discharge and of the emission is less than
rosecond, whereas the duration in Fig. 95, g, reaches
ec.
he second part of the monograph gives a detailed
w of a large number of papers on procedures of
al analysis of pure and super-pure materials. The
est as well as the most advanced methods are
here, thus presenting indeed a complete solution
problem of the determination of very low concen-
ns of impurities in materials of any kind, even
ery complex spectra. The method of fractional
lation and that of evaporation are discussed in de-
The various procedures for chemical enriching of
mples are considered in full. The whole presenta-
ncludes a large number of practical examples of
sis of various materials. The practicians of spec-
nalysis will find in these examples many helpful
stions. The methods of determination of gases in
s and in gas mixtures are considered in a separate
er. It would have been more advisable to place this
er 9 on gas analysis at the end of the second part,
the following chapters 10 and 11 continue with the
topic, dealt with in chapters 6, 7, and 8, on the
sis of metallic components.
A few remarks about this part are in order; first of
oncerning the terminology. A habit of using the preposition "on" has been established which is not proper in the Russian language. For instance "the analysis of uranium on impurities," instead of "the analysis of impurities in uranium," which is natural for the Russian language. This kind of terminology, along with the correct one, is often found in the book, as, for instance, in the titles of the sections of chapter 11. It seems to us that in a serious monograph one should be attentive to the Russian language.

Then, the frequently used term "graduating graphs" should be replaced by the term "analytical curves" that correctly describes the actual matter.

There is no uniformity with respect to references; sometimes only the number of the reference is given in the text, and sometimes also the names of the authors are given.

The photographs of the spectra leave much room for improvement. The Publishing House could have provided good and clear plates.

In discussing the chemical enriching, the danger of losses and the need for a check of the procedure is correctly stressed. It should be mentioned that the use of the method of additions removes this danger, because it makes the losses equal for the original samples and for the samples with the additions, when they are equally treated.

In the presentation of the method of transferring a solution onto the surface of a carbon electrode (p. 280), the role of adsorption in carbon should be mentioned. This role is different for different elements; this results in different depths of penetration into the electrode, and in unstable transfer of the elements into the discharge.

The third part contains the essentials of three analytical methods for determination of the isotopic composition of samples. Chapter 12 describes isotopic analysis with atomic spectra. The influence of the isotopic composition of the sample on the atomic spectra is considered here, as well as the connection between the intensity of the isotope lines and their concentration in the sample. Various examples of analysis are given. Appendix 2 contains a detailed description of the method of evaluation of tracings of narrow groups of spectral lines which usually appear in isotopic analysis. Isotopic analysis with molecular spectra is treated in the next chapter. This method is described with less details, although here also the general topics are discussed, and examples of analysis are given.

At the end of this section of the book an account is given of a special kind of isotopic analysis, namely, isotopic balancing as applied in the determination of hydrogen in metals. Here the thorough description of the detailed investigation of this method conducted by the writers, the analysis of the working of the apparatus, and of the various possible errors are very valuable. As always, the practical application of the method is pointed out.

Summarizing the review of this monograph, its appearance must be welcomed, and it should be recommended to the practicians of spectral analysis. The shortcomings mentioned here, which appear in the first part, should be corrected in following editions.

V. K. Prokof'ev

INFRARED METHODS, PRINCIPLES, AND APPLICATIONS. BY G. K. T. CONN AND D. G. AVERY.
Academic Press, New York and London, 1960. 203 pp.

(pp. 293-294)

This book represents the seventh volume of the "Physical Chemistry" monograph series, issued since 1952 by Stanford University in California. From its content and method of presentation, it is actually an introduction to infrared spectroscopy. The first part—fundamental principles—takes up three quarters of the bulk of the book and contains five chapters. The laws of thermal radiation and the properties of infrared radiation sources are considered in the first chapter; the properties of optical materials for prisms, windows, and polarizers, and the choice of cells and filters are dealt with in the second chapter. Chapter 3 is devoted to radiation detectors; here the elementary theory of thermal and semiconductor detectors is given, the fundamental relationships which determine the spectral sensitivity and noise level are derived, and graphs and a combined table of the characteristics of various detectors are given. Fundamental concepts on the layout of standard circuits and amplifier elements used to amplify the signals from infrared radiation detectors are given in chapter 4, and the dispersing optical systems of spectrometers in chapter 5 (monochromator layouts, the fundamental relationships among the elements, and the effect of diffraction formulas are derived for energy calculations and the lection of scanning speed). In conclusion, the applicat of the interference method with amplitude modulation are briefly considered.

In the four short shapters of the second part, cert practical questions of the calibration of radiation dete tors relative to black-body radiation and of the calibr tion of monochromators (by energy and by wavelength are considered; examples are given of the application of infrared spectroscopy for continuous control in industry, and the fundamentals of radiation pyrometry a set out.

The book has been provided with an author index. The bibliography contains 270 titles (in the first part) and 21 titles (in the second part).

On the whole, the book may be useful to many experimenters who wish to become acquainted with the fundamentals of infrared spectrometry.

V. A. Nikitin

INFRARED RADIATION. BY H. L. HACKFORTH
McGraw-Hill, New York, 1960. 330 pp.

(pp. 294-295)

The author states in his preface that the text is designed for university students desiring to familiarize themselves with the physical basis of infrared techniques and the various applications of infrared radiation.

The first two chapters of the first part are devoted to a historical review (chapter I) and an examination of the laws of thermal radiation and of the general principles underlying the construction of infrared systems (chapter II). The subsequent chapters deal with fundamentals, and the discussion is based on a general model of an infrared system consisting of a radiation source, the radiation of the background, the atmosphere or some other medium, the optical system, the radiation detector, and an amplifier of the detector signals. The remainder of the first part of the book is devoted to a discussion of the main properties and characteristics of the components of an infrared system, the construction of each component, and the interrelationship between them. The second part of the book gives practical examples of various types of infrared systems.

Chapter III deals with infrared radiation sources, the principles of their construction, and their characteristics. Chapter IV discusses the factors determining the transmittancy of the earth's atmosphere: absorption by water vapor, carbon dioxide, ozone, scattering by smoke and fog. Chapter V consists of a discussion optical systems and their components (lenses, mirror prisms, diffraction gratings, their properties, aberra tions of light rays, scanning methods, electron-optica amplifiers). Chapter VI contains a discussion on the properties of various optical materials in the infrare region. Chapter VII deals in adequate detail with the struction and characteristics of radiation detectors—thermopiles (PbS, PbSe, PbTe, InSb), bolometers, and optical-acoustic and germanium detectors. Chapter V the last chapter in the first part of this book, is a dis cussion of the principles governing the rational choic of various components in the design of infrared syste

The second part of Infrared Radiation gives a co prehensive review of the practical applications of inf red radiation: Chapter IX describes the diagrams of various types of instruments (radiometers, pyromete photocameras, monochromators, spectrographs, spec trometers and spectrophotometers, microscopes, tel scopes, spectroanalyzers). Chapter X is a concise d scription of the applications of infrared radiation in scientific investigations (in physics, chemistry, biolo medicine, astro- and geophysics). Chapter XI enume

he uses of infrared radiation in industry and agri-
e and its military uses. The last chapter reviews
plications of infrared radiation in investigations of
per atmospheric layers and of the cosmic space
he help of rockets and satellites.
n general the book is easy to read and is well il-
ted with diagrams, graphs, tables, and photographs.
contains significant reference material, in par-
r, very important formulas and quantitative data on
-body radiation, on absorption by atmospheric water
and carbon dioxide, on the physical properties of
l materials (also at high temperatures), on the spec-
ensitivity of detectors, and the dependence of noise
nal ratio, on temperature, time constant, amplifier
pass, area of the detector, and other parameters.
chapter has a well-selected bibliography (about 270
ences in toto).

The author's coverage of the principles of infrared techniques is adequate but his discussion of the applications of infrared radiation in various scientific investigations is very superficial (chapter X occupies only twenty pages out of the book's total of three hundred pages). In particular, only one paragraph (eight pages), is devoted to infrared spectroscopy, molecular analysis, its physical basis and its methods, subjects which, in our view, should have been given at least a chapter.

Notwithstanding some serious shortcomings, and taking into consideration the absence of similar monographs in Russian, we strongly recommend the translation of this book and its distribution for use either as a textbook or for reference.

V. A. Nikitin

OPTICAL IMAGE ASSESSMENT USING FREQUENCY RESPONSE TECHNIQUES

ceedings of a Summer School held in the Department of Physics, Imperial College, London, July 7-10, 1958).

TABLES OF OPTICAL FREQUENCY RESPONSE FOR THE CASES OF SPHERICAL ABERATION AND COMA

Technical Optics Section, Imperial College of Science and Technology, London, 1959.

(pp. 295-296)

oth of these publications are multilithed. The col-
n of summer school lectures contains 134 pages of
nd 37 pages of figures. The tables of values of con-
transmission coefficient for systems with spherical
ation and coma are appended.
n July 1958 a seminar on the problem of optical
quality was held at the Imperial College of Science
echnology, London. The publication under review
the contents of the 17 lectures presented at this
ar by investigators from various countries.
s organizer of the seminar, H. H. Hopkins success-
undertook to summarize and to give an exhaustive
ntation of the results of applying the method of op-
requency response to the evaluation of the quality
ical systems and to the study of the optical image
oherent sources. Participants in the seminar in-
l well-known specialists in optics and scientific
graphy who had been working on various facets of
roblem under consideration, and who had made sig-
nt contributions to its solution. The collected lec-
and the appended tables treat all the basic ques-
in the present knowledge of optical frequency re-
e and give a complete presentation of this knowl-
in its theoretical aspect and of the application of
ethod to the solution of practical problems.
The collection begins with a paper by Hopkins which
a short but very clear explanation of the essence
method of optical frequency response in the case
inusoidal test object. In another paper Hopkins
ares the method of optical frequency response with
ously developed methods of evaluation of images
ives formulas for passing from one system of re-
e to another.
Methods of calculating the contrast transmission
cient of systems in the presence of various aber-
ns are given in the papers of Hopkins, Goodbody, and
thay. In particular, a method of calculation using an
ronic computer is considered. Methods of calcula-
tion are given which take account of diffraction phenomena, as also are methods based only on geometrical optics.

Experimental methods of determining the contrast transmission coefficient are explained in the papers of Birch and Kelsell. The first of these papers gives a survey of existing, basically photoelectric, methods, and also describes a setup constructed by the author. The second considers an interference method of determining the contrast transmission coefficient, includes a diagram of the apparatus, and presents results of the measurements. The principle of the interference method was proposed by Hopkins.

The papers of Frieser, Vienot, and Wilszynski deal with the photographic image. They show the special nature of the applicability of the Fourier integral to the photographic image as compared with the optical one; they consider questions of the application of the method to photographic systems of the "objective-photographic plate" type and to the description of the graininess of developed photographic material, and describe experimental methods for determining Fourier spectra.

The collection contains a detailed paper by Linfoot on information theory and its application to the evaluation of optical systems.

The literature references in the lectures include almost all of the more interesting papers published in the last ten to fifteen years.

The collection will be of interest to a wide group of specialists concerned with the development and investigation of optical and photographic systems. Optical theorists, optical engineers, designers, and specialists in photographic imaging will find useful information in it. The collection will be of especially great help to persons who need to familiarize themselves quickly with the essential features of the problem under consideration.

A. Ashchechlov

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Editor: JOHN N. HOWARD, *Geophysics Research Directorate, Bedford, Mass.*

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(FILLER MATERIAL - NOT IN RUSSIAN ORIGINAL)

uration of the Photo- and Radioluminescence of Anthracene and Naphthalene Crystals . . . . . M. D. Galanin and Z. A. Chizhikova 143 (271)
he "Selectivity" of the Thermal Emission of CaO and MgO . . . . . V. A. Sokolov, A. N. Gorban, and N. A. Nazimova 144 (273)
n Infrared Electronic Transition in the Er^{3+} Ion . . . . . G. S. Krinchik and M. V. Chetkin 145 (274)
n the Differentiation of Spectra . . . . . V. A. Zubov 146 (275)
ector Coupling in X-Ray Spectra . . . . . A. M. Gutman 147 (277)
ependence of the Association of Rhodamines on the Structure of Their Molecules and the Nature of the Solvent . . . . . L. V. Levshin and I. S. Lonskaya 148 (278)
he Krishnan Effect . . . . . D. K. Beridze and M. I. Shakhparonov 150 (282)
he Free Electron Model Applied to the Thiophene Molecule . . . . . T. N. Rekasheva 152 (284)
ew Data on the Absorption Spectra of Thiazine Dye Crystals . . . . . N. M. Melankholin 153 (286)
he Effect of Nitrogen on Excited Mercury Atoms . . . . . I. Agyrbichanu, I. Kukurezyanu, V. Vasiliu, and I. Popesku 155 (289)

OOK REVIEWS

mission Analysis of Atomic Materials. By A. N. Zaidel', N. I. Kaliteevskii, L. V. Lipis, and M. P. Chaika . . . . . V. K. Prokof'ev 156 (291)
nfrared Methods, Principles, and Applications. By G. K. T. Conn and D. G. Avery . . . . . V. A. Nikitin 158 (293)
nfrared Radiation. By H. L. Hackforth . . . . . V. A. Nikitin 158 (294)
Optical Image Assessment Using Frequency Response Techniques
Tables of Optical Frequency Response for the Cases of Spherical Aberration and Coma . . . . . A. Ashchechlov 159 (295)

EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. D. B. Judd, National Bureau of Standards, Washington 25, D. C.

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CONTENTS

(Numbers in parentheses are original Russian page numbers.
These Russian page numbers are also quoted at the head of each paper.)

Calculation of $\overline{r^{-3}}(n, l)$ From the Fine Structure of Spectra . . . . . V. S. Korol'kov 73 (137)

Recurrence Formulas in the Calculations of Moments of Distributions of Transition Probabilities . . . . . O. I. Sil'd 75 (141)

Theory of Infrared Absorption Band Intensities of Complex Molecules Containing Several Identical Groups . . . . . L. A. Gribov 77 (146)

On the Theory of Line Intensities in Raman Spectra. II. The Quantum Model (Taking Account of Anharmonicity and Deviation from the Condon Approximation . L. L. Krushinskii and P. P. Shorygin 80 (151)

The Intensity of Raman Bands and the Character of the Chemical Bond . . . . . Ya. S. Bobovich 85 (161)

An Investigation of the Raman Indicatrix . . . . . I. I. Kondilenko, P. A. Korotkov, and V. L. Strizhevskii 89 (169)

Infrared Spectra of Phthalocyanines. I. The Effect of Crystalline Structure and of the Central Metallic Atom on the Phthalocyanine Molecule in the Solid State . . A. N. Sidorov and I. P. Kotlyar 92 (175)

Frequencies and Intensities of the Absorption Bands of Monosubstituted Benzenes in the Region of the Stretching Vibrations of C—$H_{arom.}$ Bonds . . . . . M. P. Lisitsa and I. N. Khalimonova 97 (185)

Shape of the Vibrational Absorption Band Contours of Liquid Chloroform and Bromoform . . . . . Yu. P. Tsyashchenko 101 (192)

The Effect of Temperature on the Infrared Spectra of Organo-Silicon Compounds. I. Crystalline Hexaethyldisiloxane . . . . . O. V. Vakulenko, G. G. Kirei, and M. P. Lisitsa 103 (196)

Evidence for Hydrogen Bonding in the Infrared Spectra of Crystalline Lithium Hydroxides . . . . . A. I. Stekhanov and E. A. Popova 107 (203)

The Effect of Foreign Gases on the Absorption of Infrared Radiation by Water Vapor . . . . . K. P. Vasilevskii 109 (207)

Certain Regularities in the Electroluminescence of ZnS:Cu:Al Phosphors with High Copper Content. . . . . A. M. Bonch-Bruevich 114 (216)

The Action of an Alternating Magnetic Field on the Propagation of Circularly Polarized Radiation in Matter . . . . . O. Ya. Savchenko 118 (223)

A Molecular Theory of Refraction of Light in Crystals . . . . . B. A. Sotskii 121 (229)

Optical Principle of Reversibility and its Application in the Theory of Thin-Layer Coatings . . . . . P. G. Kard 125 (237)

Theory of Light Reflection From a Thin Absorbing Film Deposited on a Metal . . . . . A. Vašíček 128 (242)

Accuracy of Determining Optical Constants of Absorbing Substances by Reflection in an Arrangement Using a Polarizer and Analyzer . . . . . A. P. Prishivalko 131 (248)

Precision Diffraction Gratings for Metrologic Purposes . . . . . G. N. Rassudova and F. M. Gerasimov 136 (259)

SHORT COMMUNICATIONS

The Frequency Dependence of Raman Line Intensities . . . . . I. I. Kondilenko and V. L. Strizhevskii 137 (262)

Investigation of the Initial Stages in the Onset of Electroluminescence of a ZnS:Cu:Al Phosphor . . . . . P. S. Litvinova, L. P. Rabotkina, and P. E. Ramazanov 139 (264)

Microphotometric Determination of the Quantity of Absorbing Material in Inhomogeneous Objects . . . . . A. I. Sherudilo and V. Ya. Brodskii 140 (266)

Spectral Transmission and the Inverse Problem of Scattering Theory . . . . . K. S. Shifrin and V. F. Raskin 141 (268)

(Contents continued on inside back cover)